Supramolecular Assemblies of a Bis(terpyridine) Ligand and of its [2 × 2] Grid-type Zn^{II} and Co^{II} Complexes on Highly Ordered Pyrolytic Graphite

Ulrich Ziener,[a, b] Jean-Marie Lehn,*[a] Ahmed Mourran,[b] and Martin Möller*[b]

Abstract: The synthesis and characterisation of bis(terpyridine)-derived ligands which are capable of forming [2 × 2] grid-like complexes is presented. Additional pyridine substituents on these ligands do not interfere with the complexation process. Adsorbing one of the pure ligands on highly ordered pyrolytic graphite (HOPG) shows a highly ordered structure stabilised by additional weak intermolecular C–H ⋯ N hydrogen bonds partially through the extra-pyridines as could be shown by scanning tunneling microscopy (STM) investigations. Similar adsorption experiments with one of the corresponding [2 × 2] Co^{II} grid-type complexes on graphite, led also to a well-organised structure with interdigitation of the extra-pyridine moieties.

Keywords: cobalt · coordination chemistry · scanning probe microscopy · supramolecular chemistry · zinc

Introduction

Molecular self-organisation and self-assembly to supramolecular structures is the basis for the construction of new functional materials and nanoobjects in a bottom-up strategy.[1] Coordinating tailor-made ligands to appropriate metal atoms opens a wide range of structural variations of such entities which manifests itself in a vast number of investigations in this field. Helices, cages, ladders and grids are examples of designed sophisticated molecular structures. The metal atoms present in these complexes can confer special (e.g., magnetic or electronic) properties to them.[2, 3] Gaining technological advantage by building up devices from these compounds requires the assembly of such supramolecular tectons in a sequential, hierarchical fashion to generate even more complex nanostructures. A rational approach to such functional supramolecular nanostructures requires mastering the multiple and competing interactions, for example van der Waals forces, ionic interactions, hydrogen and coordinative bonding. The latter are especially useful for this purpose as they exhibit strong directionality and selectivity.[4, 5] In addition, entropic effects also provide a significant contribution in structure formation, for example hydrophobic (or solvophobic) effects, depletion forces, and configurational entropy. Adsorption and two-dimensional (2D) ordering of a molecular monolayer on a structurally defined substrate provides unique insight into the interaction of different components in bulk assemblies. Scanning tunneling microscopy (STM) is an appropriate tool to investigate such structures arranged on surfaces on atomic size scale. In a previous paper we reported on a [2 × 2] bis(bipyridine)pyrimidine grid complex, in which STM allowed us to observe how a variation in the molecular structure can effect the molecular orientation towards the substrate within the regular arrangement.[6]

Herein we describe the synthesis of tailored bis(terpyridine)-derived ligands containing two coordination subunits which self-assemble with Zn^{II} and Co^{II} ions to give [2 × 2] grid-like complexes, as shown earlier for the "parent" complexes.[7] The ligands have been substituted with extra-pyridines for second-level interactions with further metal ions. Additionally, they are able to form weak intermolecular C–H ⋯ N hydrogen bonds. One of these ligands was adsorbed on graphite and investigated by STM and showed highly ordered two-dimensional arrays. The [2 × 2] grid-like Co complex formed by this ligand was adsorbed on graphite, too, and yielded also a quite well arranged two-dimensional structure. Such arrays may help in the development of new approaches for storage devices for molecular electronics based on addressable single components in a highly ordered superstructure.

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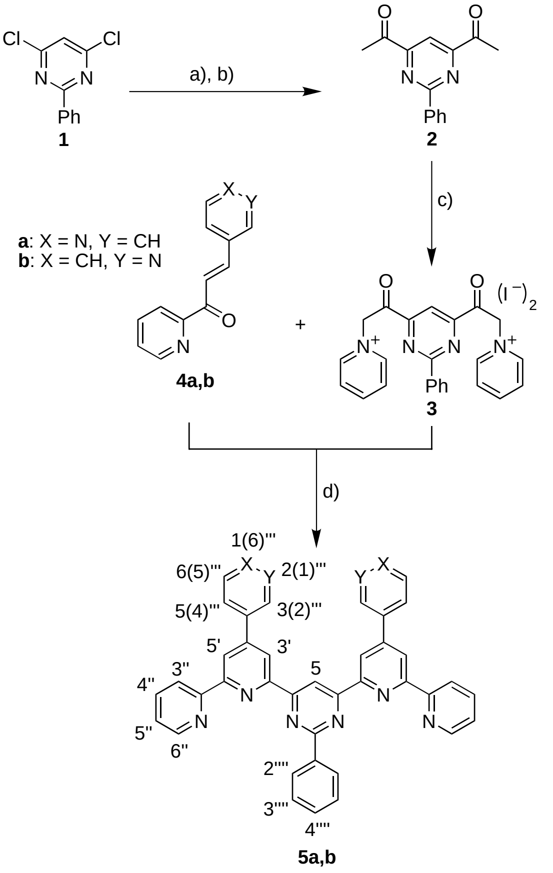
Results and Discussion

Synthesis

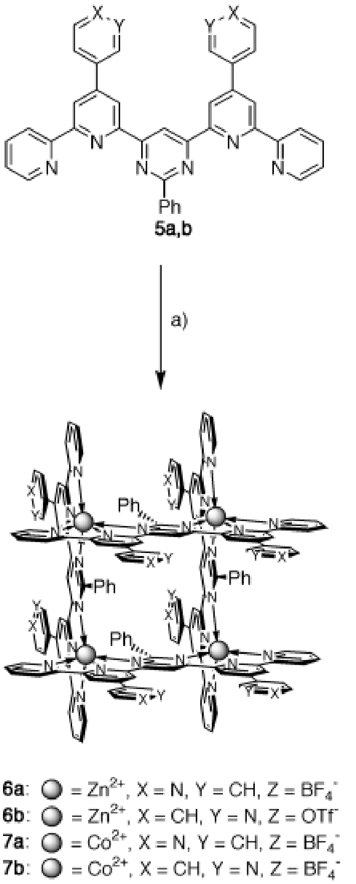
The ligands **5a, b** were synthesised by a ring-closure reaction corresponding to the Kröhnke synthesis (Scheme 1).[8] Stille coupling of **1** with (1-ethoxy)vinyltributylstannane and hydrolysis of the divinyl ether led to the diketone **2**, which could be easily converted to the bispyridinium salt **3**. The synthesis of the unsaturated ketones **4a, b** by a Knoevenagel condensation of 3- and 4-pyridine carbaldehyde, respectively, with 2-acetyl pyridine has been described previously.[9] The double Michael addition of **3** to **4a** and **4b**, respectively, followed by cyclisation and aromatisation gave the bis(terpyridine) derivatives **5a** and **5b** in good yields.



Scheme 1. Syntheses of the ligands **5a** and **5b**, a) (1-ethoxy)vinyltributylstannane, $[Pd(PPh_3)_2Cl_2]$, DMF, b) acetone, HCl, c) pyridine, iodine, d) MeOH, NH_4OAc. The numbering relates to the assignment of the signals in the ^1H NMR spectra (the numbers in parentheses refer to **5b**).

The corresponding grid-like complexes **6** and **7** were obtained by reacting the ligands **5a**, **b** with Zn^{II} and Co^{II} salts, respectively (Scheme 2).

^1H NMR spectroscopy of **6a** and **6b** is consistent with the proposed structure of the complexes. The spectra of the ligands **5a, b** show signals between about $\delta = 7.4$ and 9.8 and are rather complicated due to superposition of several groups of signals. Complexation with Zn^{II} leads to a spreading out of the peaks and to the appearance of five new signals at relatively high field up to about $\delta = 5.5$. They can be assigned to the five phenyl protons,[7] indicating that the free rotation of a phenyl group is frozen and the ring plane is perpendicular to the plane of the terpyridine groups of the two orthogonal ligands (see Scheme 2, **6a, b**). These spectral features are similar to those observed earlier for the corresponding "parent" complexes, whose structure had also been confirmed by X-ray crystallography.[7, 10] The strong high-field shift of the phenyl protons is caused by the influence of the ring current of the parallel aligned terpyridine units on the phenyl protons. Furthermore, the number of signals is indicative for the maintenance of the C_{2v} symmetry of the ligands **5a, b** in **6a** and **6b**, respectively. The formation of a linear polymeric structure is excluded by electrospray (ES) mass spectrometry which shows only signals of the tetranuclear complex with different numbers of anions.



Scheme 2. Formation of the tetranuclear grid-like complexes **6** and **7**, a) MZ_2, acetonitrile ($M = Zn^{2+}$, Co^{2+}; $Z = BF_4^-$, OTf^-).

The ^1H NMR spectra of the Co complexes **7a, b** are quite different from the previous spectra. The spectrum of **7a** shows fourteen singlets covering a range of almost 350 ppm, which is related to the paramagnetism of Co^{II}. Like in the case of **6a, b** the five protons of the phenyl ring are discriminated. From the number of the signals it can be again concluded that the C_{2v} symmetry of the ligands **5a, b** is maintained. The strongly high-field shifted signals can be assigned to the phenyl protons by comparison with the spectral data of related complexes.[7, 11] The ^1H NMR spectrum of **7b** is similar to that for **7a**. According to the proposed structure, sixteen ^1H NMR signals are expected to be resolved, but only fifteen signals are

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observed. Integration indicates that the signal at $\delta = 16.6$ is caused by two different protons.

The unsatisfying elemental analysis data are not unusual for metal complexes and incomplete combustion.[12] Furthermore, it must be expected that some complexes may contain water bound to the non-coordinated N atoms of the pyridine rings as it is assumed for **7a** (see Experimental Section).

Investigations by scanning tunneling microscopy (STM)

In situ adsorption of the ligand 5a on highly ordered pyrolytic graphite (HOPG) surface: Figure 1a depicts a typical large scan area STM image of a monofilm of ligand **5a** adsorbed on a HOPG surface.

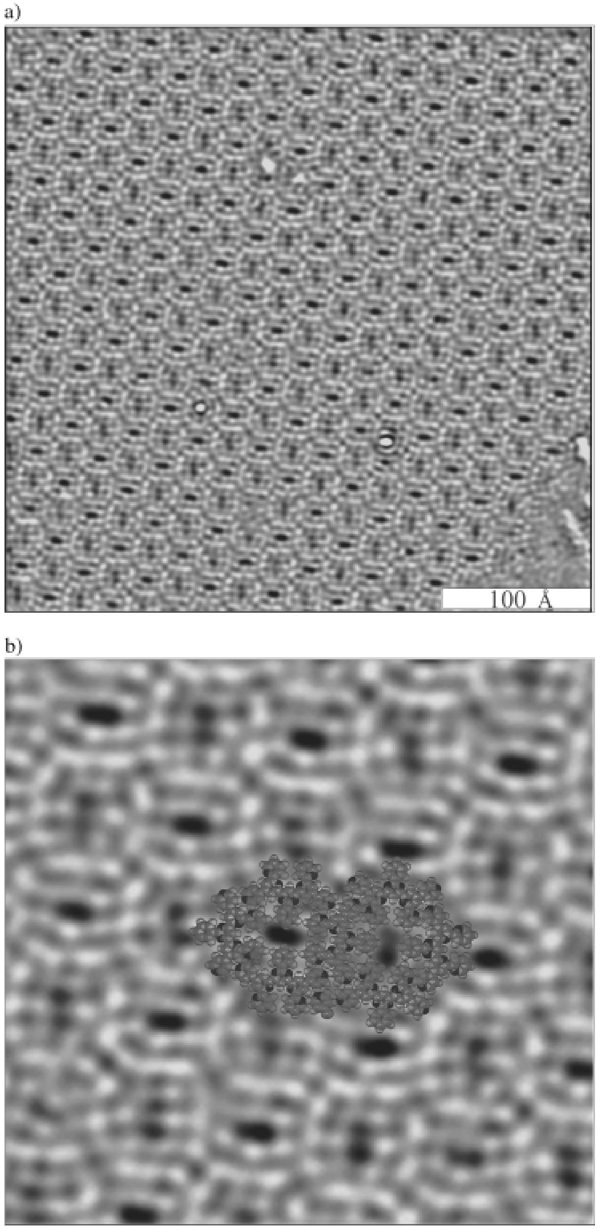
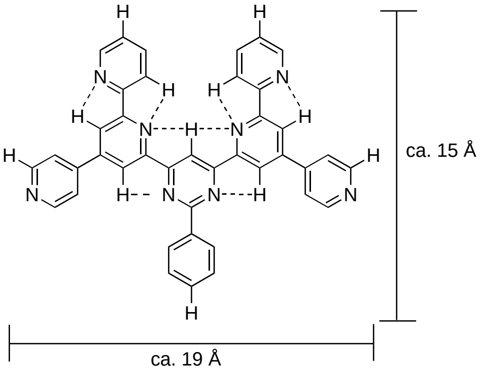


Figure 1. Fourier-filtered STM image of **5a** on graphite: a) large scan area, b) magnified detail with a model of the ligand showing the geometric agreement between model and experimental results.

The enlargement in Figure 1b shows well-resolved details of the highly ordered rectangular structure with ellipsoidal directionally alternating voids. The repeating motif is formed by discrete light spots with a diameter of about 3 to 4 Å. The two-dimensional unit cell is of square symmetry (plane group *p*4), containing four molecules. The lattice constants were determined to be $A = 20 \pm 2$ Å. A model of the molecular arrangement of **5a** on HOPG derived from the STM pictures is depicted in Scheme 3, where the molecule is represented in its lowest energy form, having all NC–CN rotamers in *N*,*N*-transoid orientation. The size of an individual molecule measured by STM is in agreement with the dimensions determined by single-crystal X-ray analysis of similar compounds.[7, 13]

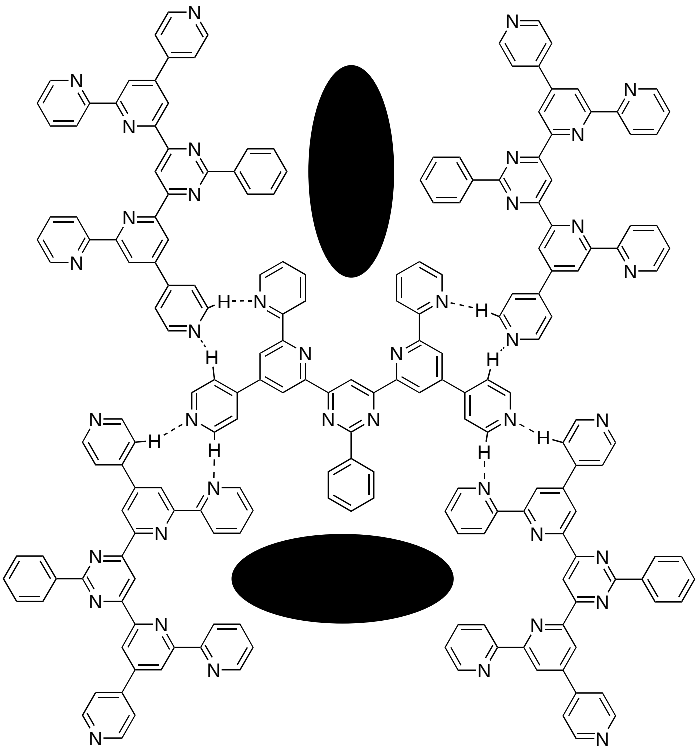


Scheme 3. Ligand **5a** in the transoid NC–CN conformation with weak intramolecular C–H ··· N hydrogen bonds (dashed lines).

Several arguments support our model, 1) the graphite surface favors the planar arrangement of the (hetero)aromatic moieties;[14] 2) oligopyridines and related compounds adopt in solution as well as in the solid state a NC–CN transoid conformation due to repulsive forces of the lone pairs of the nitrogen atoms and weak intramolecular hydrogen bonds (Scheme 3);[15, 16] 3) this transoid conformation allows the formation of eight weak intermolecular hydrogen bonds per molecule which provide the stability of the 2D assembly (Scheme 4). Thus, the ellipsoidal voids in the monomolecular assembly of the ligand **5a** on HOPG appear as a consequence of the intra- and intermolecular interaction of the ligand in the vicinity of the HOPG surface.

2D assembly of the [2 × 2] grid-like Co^{II} complex 7a on HOPG: Figure 2a shows a representative STM image of the Co^{II} complex **7a** on HOPG. The large scan image depicts boundaries between different domains. The angle between domain directions is 120 ± 3°, corresponding to the hexagonal graphite symmetry. The poor resolution of the image is due to the low adherence of the complex on the HOPG surface. Indeed, the molecules were easily removed from the scanning area after two to four scans. Yet, the images were well reproducible. The analysis of the STM images has been done by taking into account the effects discussed above.

The structure of the monolayer of complex **7a** on HOPG (Figure 2b) is manifestly distinct from that of ligand **5a** (Figure 1). The lattice constants of the 2D structure of **7a**



Scheme 4. Proposed model for the arrangement of **5a** on a graphite surface stabilised by weak intermolecular hydrogen bonds (dashed lines).

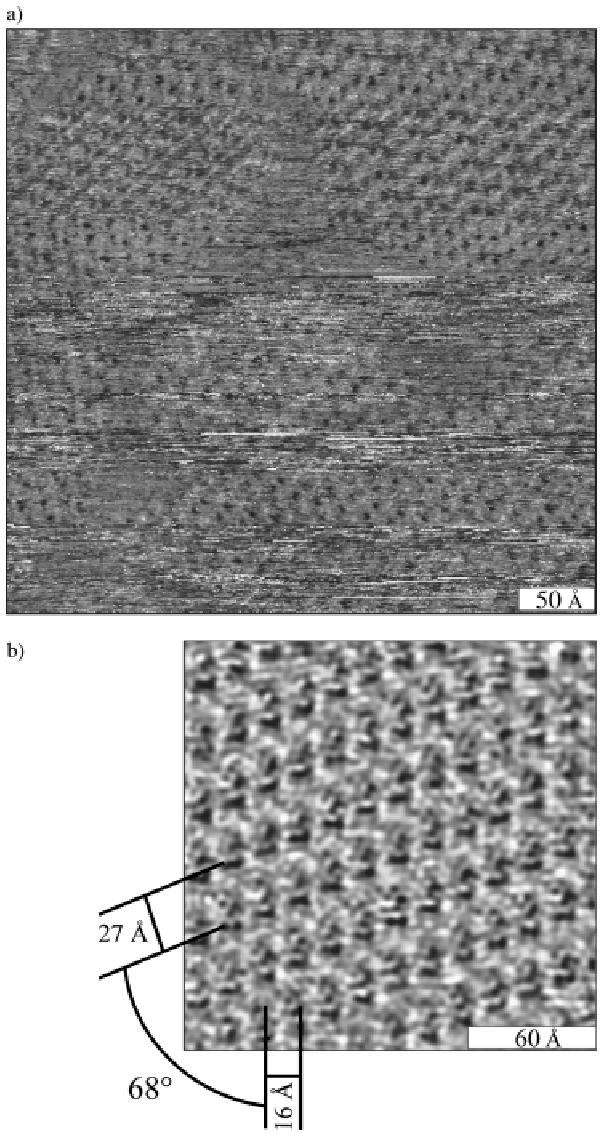


Figure 2. Fourier-filtered STM image of **7a** on graphite: a) large scan area, b) detailed view.

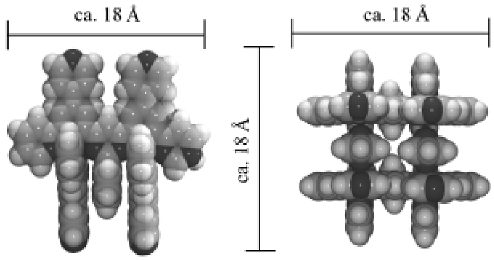


Figure 3. Proposed structure for a single molecule of **7a**, (left) side view; (right) top view. The sizes of the spheres are 2/3 of the correct van-der-Waals radii for clarity reasons. The dimensions are deduced from single-crystal X-ray structures of related complexes.[7]

were determined to be $A = 16 \pm 2$ Å, $B = 27 \pm 2$ Å and $\Gamma = 68 \pm 3°$.

Based on the X-ray analysis of the similar bis(bipyridine) pyrimidine complexes, without the extra pyridine moieties sticking out at the top and bottom of the complex, we assume an approximately cubic shape with edges of 18 Å for **7a** (Figure 3).[2, 7] This is not obviously consistent with the STM data. So far the poor resolution of the STM images of **7a** does not allow a rigorous interpretation. Some features may be explained qualitatively as follows: STM investigations of similar grid complexes on graphite[6] indicated that the square grid complexes were either "sitting" with the C_2 axis perpendicular or "lying" with the C_2 axis parallel to the substrate surface depending on the substituents at the ligands. In both cases the directions of the main periodicities in the STM images were orthogonal.[6] The deviation from orthogonality found for the 2D lattice in Figure 2 might either arise from an unlikely distortion of the complexes themselves or from intercalation from adjacent complexes. Distortion of the complex would imply a strong local distortion of the octahedral coordination sphere of the Co ions. Intercalation of neighboring complexes decreases the periodicity in one direction consistent with the 16 Å period. Such intercalative insertion is compatible with the thickness of the ligand units and their distances in the grids. Insertion of benzene solvent molecules between ligands in grid-type complexes has been observed.[17] The 27 Å period in the other direction must then be constituted by couples of two complexes. Based on this consideration we suggest the structural arrangement of **7a** on graphite shown in Figure 4. Though the periodicities (ca. 17 and 31 Å) are somewhat too large, the angle (ca. 67°) between the two main axes of this monofilm structure fits well the STM results. Packing of the complexes as depicted in Figure 4 will gain from weak intramolecular $N\cdots H{-}C$ hydrogen bonds as well as from edge-to-face and face-to-face interactions of the aromatic rings which are well known for the solid-state structures of bis(terpyridine) complexes.[18] In the proposed

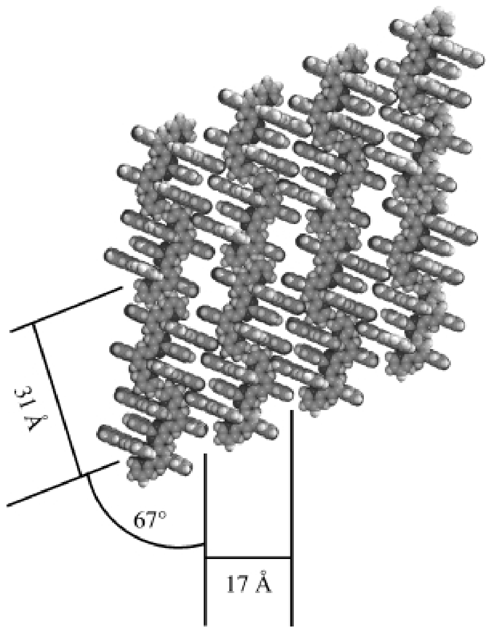


Figure 4. Suggested model for the arrangement of **7a** on a graphite surface. The sizes of the spheres are 2/3 of the correct van-der-Waals radii for clarity reasons.

arrangement the mirror planes of the complexes are parallel to the substrate. An inclination of these planes with respect to the surface would allow an even stronger intercalation of the complexes and so decrease the distances, but such details cannot be deduced from the image.

Conclusion

Two new ligands containing two terpyridine-type coordination subunits and each substituted by an additional pyridine unit have been synthesised and studied. One of them was adsorbed as a monofilm on HOPG and found to yield a well-defined rather peculiar 2D structure involving intra- and inter-molecular C–H ⋯ N interactions of the molecules.

The distinct changes of the monofilm structure that were observed by STM after complexation of Zn^{II} and Co^{II} ions, are in agreement with the expected formation of [2 × 2] grid-like complexes. STM experiments on one of the Co complexes revealed a weaker adsorption on HOPG than observed earlier for the corresponding parent complex.[6] In the case of the pure organic ligand a coplanar arrangement of the aromatic rings and the graphite surface stabilises the structure, whereas the orthogonal coordination of the metal ion in the complexes does not allow the face-on π bonding of the aromatic rings on the graphite surface. In this case the adsorption is facilitated by the interaction of the N atoms of the *exo* pyridine rings with the graphite. For metallic surfaces like gold or silver, it is expected that an attractive interaction would enhance the stability and binding to the surface. Experiments on the adsorption of the present complexes on gold are underway. The ability to control and manipulate such arrangements could provide approaches to locally addressable, inorganic storage devices for molecular electronics.

Experimental Section

General: 2-Phenyl-4,6-dichloropyrimidine (**1**),[19] (1-ethoxy)vinyltributylstannane,[20] and the ketones **4a** and **4b**[9] were prepared according to the literature. If water-free solvents were used, they were dried according to reference [21]. The other reagents and solvents were used without further purification. The NMR data were obtained on a Bruker AC 200 spectrometer at 200.1 MHz (^1H) and 50.2 MHz (^{13}C), respectively, calibrated against the solvent signal ($CDCl_3$): ^1H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.0$; $[D_6]$DMSO: ^1H NMR: $\delta = 2.50$; ^{13}C NMR: $\delta = 39.9$; $[D_3]$acetonitrile: ^1H NMR: $\delta = 1.94$) and are given in ppm. Fast atom bombardment (FAB) mass spectrometry was performed on a ZAB-HF VG spectrometer with *m*-nitrobenzyl alcohol as the matrix and electrospray (ES) mass spectra were recorded on a triple quadrupole mass spectrometer Quattro II (Micromass).

STM investigations: STM measurements were carried out at ambient conditions with a low-current RHK 1000 control system. STM imaging of the ad-layers was performed at the internal interface between HOPG and a concentrated solution of the ligand **5a** dissolved in 1,2,4-trichlorobenzene. A drop of solution was placed on a freshly cleaved HOPG surface, while the surface had already been scanned by STM under conditions that allowed atomic resolution of the graphite surface structure. A potential of $U = \pm 1$ V was applied to the substrate. The scan rate was varied between 0.2 and 0.6 $\mu m\,s^{-1}$. The tunneling current set point was 8–20 pA. All images presented were obtained at constant current mode using a Pt/Ir (90/10) tip, which was mechanically sharpened.

The Co complex **7a** was dissolved in acetonitrile at a concentration less than 1 wt %. A droplet of the solution was deposited on a freshly cleaved surface of graphite. The substrates were dried in the presence of acetonitrile vapor over 1 h (in a covered Petri dish with a few mL of acetonitrile aside the sample). Then the sample was taken out of the Petri dish and dried fully under ambient conditions. The molecular structure of the layer was probed by STM under atmospheric conditions.

2-Phenyl-4,6-diacetylpyrimidine (1): 2-Phenyl-4,6-dichloropyrimidine (1.00 g, 4.4 mmol) was mixed with (1-ethoxy)vinyltributylstannane (3.61 g, 10 mmol) and $[Pd(PPh_3)_2Cl_2]$ (290 mg, 0.4 mmol), dissolved in dry DMF, and degassed with argon. The solution was stirred at 80 °C for 19 h during which time it turned black. After the solution had been cooled to ambient temperature it was poured into a mixture of KF (1 g) in water and diethyl ether. The slurry was stirred for 15 min and the off-white solid filtered and washed with diethyl ether. The aqueous phase was separated from the organic phase and extracted three times with diethyl ether. The combined organic phases were dried ($MgSO_4$) and the solvent removed. The resulting crude brown solid of 2-phenyl-4,6-bis(1-ethoxyvinyl)pyrimidine (1.30 g 4.4 mmol) was dissolved in a mixture of acetone (15 mL) and 2 N HCl (2 mL) and stirred at room temperature for 20 h. The bulky off-white precipitate formed was filtered, washed with a little acetone, and dried in vacuo. Yield: 895 mg (85 % over two steps). M.p. 133 °C. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 8.60-8.55$ (m, 2H; H_{ortho}), 8.27 (s, 1H; H_5), 7.58–7.51 (m, 3H; $H_{meta,para}$), 2.83 (s, 6H; $2CH_3$); ^{13}C NMR (50.2 MHz, $CDCl_3$): $\delta = 198.7$, 165.0, 161.2, 136.0, 131.7, 128.7, 128.3, 110.6, 25.5; MS (FAB): *m/z*: 241 $[M+H^+]$; elemental analysis calcd (%) for $C_{14}H_{12}N_2O_2$ (240.3): C 69.99, H 5.03, N 11.66; found: C 70.15, H 4.80, N 11.68.

Bispyridinium salt 3: Iodine (1.056 g, 4.16 mmol) in dry pyridine (3.5 mL) was added to a solution of 2-phenyl-4,6-diacetylpyrimidine (**1**) (500 mg, 2.08 mmol) in dry pyridine (2.5 mL), and the deeply coloured mixture was stirred at 100 °C for 4 h. It was cooled to room temperature and stirred overnight. The golden-brown precipitate was filtered and washed with dry EtOH until the liquid became colourless. The golden-brown solid was dried in vacuo. Yield: 1.047 g (77 %). M.p. above 210 °C darkening, above 220 °C melting with decomposition. ^1H NMR (200 MHz, $[D_6]$DMSO): $\delta = 9.03$ (d, $J = 6$ Hz, 4H; $H_{2',6'}$), 8.83–8.73 (m, 4H; $H_{4',ortho}$), 8.34 (t, $J = 7$ Hz, 4H; $H_{3',5'}$), 8.16 (s, 1H; H_5), 7.77–7.73 (m, 3H; $H_{meta,para}$), 6.75 (s, 4H; $2CH_2$); ^{13}C NMR (50.2 MHz, $[D_6]$DMSO): $\delta = 190.5$, 164.1, 159.5, 146.6, 146.2, 134.7, 132.6, 129.2, 128.4, 127.8, 110.3, 66.4; MS (FAB): *m/z*: 523 $[M-I]^+$, 395 $[M-2I-H]^+$, 317 $[M-2I-\text{pyridine}]^+$; elemental analysis calcd (%) for $C_{24}H_{20}N_4O_2I_2$ (650.3): C 44.33, H 3.10, N 8.62; found: C 44.57, H 3.21, N 8.67.

Ligand 5a: Bispyridinium salt **3** (356 mg, 0.55 mmol), ketone **4a** (230 mg, 1.09 mmol) and NH_4OAc (2.0 g, 26 mmol) in MeOH (10 mL) were heated under reflux. The mixture formed readily a homogeneous solution and after 1 min an off-white precipitate. The suspension was kept under reflux for 1 h and after the mixture had been cooled, the solid was filtered, washed two times with MeOH and dried in vacuo. Yield: 242 mg (71 %). M.p. above 275 °C slow decomposition. ^1H NMR (200 MHz, $CDCl_3$):[22] $\delta = 9.66$ (s, 1 H; H_5), 8.89 (d, $J = 2$ Hz, 2 H; $H_{3'}$), 8.82 – 8.66 (m, 12 H; $H_{ortho,5',3'',6'',2''',6'''}$), 7.85 (td, $J = 8$, 2 Hz, 2 H; $H_{4''}$), 7.79 (dd, A part of AB system, $J = 4$, 2 Hz, 4 H; $H_{3''',5'''}$), 7.60 – 7.53 (m, 3 H; $H_{meta,para}$), 7.39 (ddd, $J = 7$, 5, 1 Hz, 2 H; $H_{5''}$); ^{13}C NMR (50.2 MHz, $CDCl_3$): $\delta = 163.6$, 163.0, 155.9, 155.0, 154.0, 150.5, 149.0, 146.8, 145.2, 137.1, 136.3, 130.8, 128.4, 128.2, 124.0, 121.4, 121.0, 119.6, 118.5, 111.3; high-resolution MS (FAB): calcd (*m/z*) for $C_{40}H_{27}N_8$ $[M+H]^+$: 619.235868; found: 619.235501

Ligand 5b: Bispyridinium salt **3** (350 mg, 0.54 mmol), ketone **4b** (226 mg, 1.08 mmol) and NH_4OAc (2.0 g, 26 mmol) in MeOH (8 mL) were heated under reflux. The homogeneous solution formed an off-white precipitate after 15 min. The suspension was kept under reflux for 16 h and after the mixture had been cooled, the solid was filtered, washed two times with MeOH and dried in vacuo. Yield: 233 mg (70 %). M.p. above 275 °C darkening, 295 – 305 °C melting. ^1H NMR (200 MHz, $CDCl_3$):[22] $\delta = 9.77$ (s, 1 H; H_5), 9.20 (d, $J = 2$ Hz, 2 H; $H_{2'''}$), 9.01 (d, $J = 2$ Hz, 2 H; $H_{3'}$), 8.90 – 8.74 (m, 10 H; $H_{ortho,5',3'',6'',6'''}$), 8.23 (ddd, $J = 8$, 2, 2 Hz, 2 H; $H_{4'''}$), 7.93 (td, $J = 7$, 2 Hz, 2 H; $H_{4''}$), 7.62 – 7.57 (m, 3 H; $H_{meta,para}$), 7.52 (dd, $J = 8$, 5 Hz, 2 H; $H_{5'''}$), 7.43 (ddd, $J = 7$, 5, 1 Hz, 2 H; $H_{5''}$); ^{13}C NMR: too insoluble; high-resolution MS (FAB): calcd (*m/z*) for $C_{40}H_{27}N_8$ $[M+H]^+$: 619.235868; found: 619.235197

Zinc(II) complex 6a: Ligand **5a** (18.5 mg, 30 µmol) and $Zn(BF_4)_2 \cdot 6H_2O$ (10.4 mg, 30 µmol) were mixed in acetonitrile (5 mL), and refluxed for 5 min. This led to a pinkish solution which was stirred at room temperature for 2 h. Diethyl ether was added to precipitate the desired compound as a brownish powder which was collected by centrifugation and dried in vacuo. Yield: 17.6 mg (69 %). ^1H NMR (200 MHz, $[D_3]$acetonitrile):[22] $\delta = 9.70$ (s, 4 H; H_5), 9.33 (s, 8 H; $H_{3'}$ or $H_{5'}$), 9.05 (d, $J = 5$ Hz, 16 H; $H_{2''',6'''\,\mathrm{or}}$ $H_{3''',5'''}$), 8.81 (s, 8 H; $H_{3'}$ or $H_{5'}$), 8.42 (d, $J = 8$ Hz, 8 H; $H_{3''}$), 8.19 (d, $J = 6$ Hz, 16 H; $H_{2''',6'''}$ $_{\mathrm{or}}$ $H_{3''',5'''}$), 7.98 (td, $J = 8$, 2 Hz, 8 H; $H_{4''}$), 7.32 (t, $J = 8$ Hz, 4 H; $H_{3''''o}$), 7.17 (dd, $J = 7$, 5, Hz, 8 H; $H_{5''}$), 7.00 (d, $J = 4$ Hz, 8 H; $H_{6''}$), 6.87 (t, $J = 7$ Hz, 4 H; $H_{4''''}$), 6.34 (t, $J = 7$ Hz, 4 H; $H_{3''''i}$), 5.95 (d, $J = 8$ Hz, 4 H; $H_{2''''o}$), 5.50 (d, $J =$ 7 Hz, 4 H; $H_{2''''i}$); MS (ES): *m/z*: 3258 $[M - 2BF_4]^+$, 3170 $[M - 3BF_4]^+$, 3084 $[M - 4BF_4]^+$; elemental analysis calcd (%) for $C_{160}H_{104}N_{32}B_8F_{32}Zn_4$ (3430.8): C 51.36, H 2.67, N 11.41; found: C 51.12, H 2.89, N 11.36.

Zinc(II) complex 6b: Ligand **5b** (8.4 mg, 13.6 µmol) and $Zn(OTf)_2$ (5.0 mg, 13.6 µmol) were mixed in acetonitrile (1 mL) and refluxed for 5 min. This led to a pinkish solution which was stirred at room temperature for 2 h. When diethyl ether was added, almost no precipitation was observed. The solution became just slightly opaque. The solvent was removed and the brownish residue dried in vacuo. Yield: 8.1 mg (61 %). ^1H NMR (200 MHz, $[D_3]$acetonitrile):[22] $\delta = 9.76$ (s, 4 H; H_5), 9.46 (d, $J = 2$ Hz, 8 H; $H_{2'''}$), 9.36 (s, 8 H; $H_{3'}$ or $H_{5'}$), 8.96 (dd, $J = 5$, 2 Hz 8 H; $H_{6'''}$), 8.81 (s, 8 H; $H_{3'}$ or $H_{5'}$), 8.68 (dd, $J = 8$, 2 Hz, 8 H; $H_{4'''}$), 8.44 (d, $J = 8$ Hz, 8 H; $H_{3''}$), 7.97 (td, $J = 8$, 2 Hz, 8 H; $H_{4''}$), 7.78 (dd, $J = 7$, 2 Hz, 8 H; $H_{5''\mathrm{or}5'''}$), 7.55 (t, $J = 8$ Hz, 4 H; $H_{3''''o}$), 7.16 (dd, $J = 7$, 5 Hz, 8 H; $H_{5''\mathrm{or}5'''}$), 7.00 (d, $J = 4$ Hz, 8 H; $H_{6''}$), 6.93 (t, $J = 7$ Hz, 4 H; $H_{4''''}$), 6.40 (t, $J = 7$ Hz, 4 H; $H_{3''''i}$), 5.97 (d, $J = 8$ Hz, 4 H; $H_{2''''o}$), 5.47 (d, $J = 7$ Hz, 8 H; $H_{2''''i}$); MS (ES): *m/z*: 3780 $[M - OTf]^+$, 3631 $[M - 2OTf]^+$, 3481 $[M - 3OTf]^+$, 3331 $[M - 4OTf]^+$, 3184 $[M - 5OTf]^+$; elemental analysis calcd (%) for $C_{168}H_{104}N_{32}F_{24}O_{24}S_8Zn_4$ (3928.8): C 51.36, H 2.67, N 11.41; found: C 53.19, H 2.78, N 11.53.

Cobalt(II) complex 7a: Ligand **5a** (50.0 mg, 81 µmol) and $Co(BF_4)_2 \cdot 6H_20$ (27.5 mg, 81 µmol) were mixed in acetonitrile (8 mL) to give a brown solution which was stirred at room temperature for one day. Diethyl ether was added to precipitate the desired complex as a brown powder which was collected by centrifugation and dried in vacuo. Yield: 63.0 mg (92 %). ^1H NMR (200 MHz, $[D_3]$acetonitrile): $\delta = 231.9$, 160.3, 130.2, 69.0, 52.9, 46.8, 23.0, 17.4, 13.2, 6.2, −16.5, −23.7, −107.1, −112.2; MS (ES): *m/z*: 3232 $[M - 2BF_4]^+$, 3145 $[M - 3BF_4]^+$, 3058 $[M - 4BF_4]^+$, 2970 $[M - 5BF_4]^+$, 2884 $[M - 6BF_4]^+$; elemental analysis calcd (%) for $C_{160}H_{104}N_{32}B_8Co_4F_{32} \cdot 8H_2O$ (3549.1): C 54.15, H 3.41, N 12.63; found: C 54.07, H 3.29, N 12.46.

Cobalt(II) complex 7b: Ligand **5b** (6.9 mg, 11 µmol) and $Co(BF_4)_2 \cdot 6H_20$ (3.8 mg, 11 µmol) were mixed in acetonitrile (1 mL) and refluxed for 5 min. This led to a brown solution which was stirred at room temperature for 2 h. Diethyl ether was added to precipitate the desired complex as a brown powder which was collected by centrifugation and dried in vacuo. Yield: 8.5 mg (89 %). ^1H NMR (200 MHz, $[D_3]$acetonitrile): $\delta = 228.9$, 160.6, 131.9, 70.3, 52.8, 45.3, 24.9, 24.3, 16.6, 15.0, 7.3, −16.7, −22.1, −108.8, −114.7; MS (ES): *m/z*: 3318 $[M - BF_4]^+$, 3231 $[M - 2BF_4]^+$, 3145 $[M - 3BF_4]^+$, 3058 $[M - 4BF_4]^+$, 2970 $[M - 5BF_4]^+$; elemental analysis calcd (%) for $C_{160}H_{104}N_{32}B_8Co_4F_{32}$ (3405.0): C 56.44, H 3.08, N 13.16; found: C 57.26, H 3.32, N 13.46.

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