

Two Morphologies of Stable, Highly Ordered Assemblies of a Long-Chain-Substituted $[2 \times 2]$ -Grid-Type Fe^{II} Complex Adsorbed on HOPG

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The programmed self-assembly of a multimetallic grid-type supramolecular architecture and its hierarchical organization on graphite are described. The doubly functionalized 4,6-bis(2,2'-bipyridyl-6-yl)-2-phenylpyrimidine derivative **1**, equipped with $\text{CH}_2\text{OC}_{16}\text{H}_{33}$ moieties at the terminal pyridine rings, was designed as a new bis(tridentate) ligand and synthesized using Stille-type coupling reactions. Treatment of ligand **1** with $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in $\text{CHCl}_3/\text{CH}_3\text{CN}$ led to the spontaneous formation of a $[2 \times 2]$ -grid-type Fe^{II} complex **2** in quantitative yield. The self-assembled tetranuclear complex **2** was adsorbed onto highly oriented pyrolytic graphite (HOPG) and studied by scanning tunneling microscopy (STM), which showed two morphologies of highly ordered two-dimensional arrays of the metallo-supramolecular archi-

tectures. The resulting monolayers of the grid-type complex **2** are much more stable than that obtained from the corresponding unsubstituted grid-type complex owing to the additional attractive forces between the hexadecyl moieties in **2** and the HOPG surface. Moreover, the reproducibility of the STM images of the hexadecyl-substituted grid **2** was strongly improved compared to the unsubstituted one. These results suggest that the introduction of long alkyl chains into metallo-supramolecular architectures would have general advantages for their organization and STM investigation on HOPG. Details of the preparation and the STM investigation of ligand **1** are also presented.

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Introduction

The design and formation of ordered nanoscaled structures with functional properties have attracted considerable attention in materials science and nanotechnology.^[1] A bottom-up approach based on the self-assembly of simple building units to nanometric-size objects is expected to be a powerful tool, instead of microfabrication as a top-down approach, for producing functional materials with great technological advantages. Especially interesting is a sequential application of different self-organization principles for the preparation of hierarchically structured materials. This would be realized by the controlled use of relatively strong, directional interactions (such as hydrogen bonds and coor-

dinative interactions) as well as weak, nondirectional interactions (such as van der Waals force and hydrophobic interaction). In this study we examined the hierarchical organization of a self-assembled multimetallic supramolecular architecture on graphite.

We have previously shown that the self-assembly of bis(tridentate) ligands, based on terpyridine-like binding sites, with octahedrally coordinated metal ions such as Fe^{II} , Co^{II} , and Zn^{II} leads to $[2 \times 2]$ -grid-type complexes.^[2–4] These complexes present interesting electronic, redox, and magnetic properties such as electronic interactions between the metal centers,^[2] multilevel electrochemical reduction up to 10 reversible steps,^[5] antiferromagnetic transition at low temperatures,^[6] and spin crossover phenomena triggered by temperature, pressure, and light.^[7] For technological application a further 2D or 3D ordering of these supramolecular complexes is required. Several strategies have been examined to obtain such ordered arrangement of the grid-type supramolecular architectures, including self-assembly at the air-water interface,^[8] hydrogen-bonded crystal formation,^[9] and adsorption on graphite.^[10,11] An excellent method to visualize such assemblies with submolecular resolution on for example highly oriented pyrolytic graphite (HOPG) is represented by scanning tunneling microscopy (STM).^[12] However, the stabilities of the monolayers obtained from unsubstituted $[2 \times 2]$ -grid-type complexes^[10] and its pyridyl-

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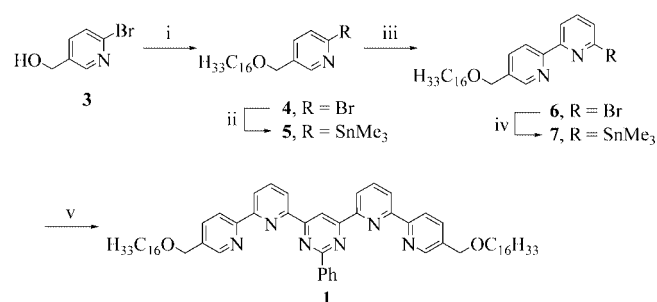
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substituted derivatives^[11] are low, and thus their STM images are obtained only with low reproducibility. To address these problems, we have designed as a new ligand 4,6-bis(2,2'-bipyridyl-6-yl)-2-phenylpyrimidine (**1**), equipped with $\text{CH}_2\text{OC}_{16}\text{H}_{33}$ moieties at the terminal pyridine rings. The long alkyl chains are expected to result in better adsorption on graphite.^[13] Herein, we describe the details of the nanopatterning of HOPG by the long-chain-substituted $[2 \times 2]$ -grid-type complex **2**, together with the preparation and STM investigation of ligand **1**.

Results and Discussion

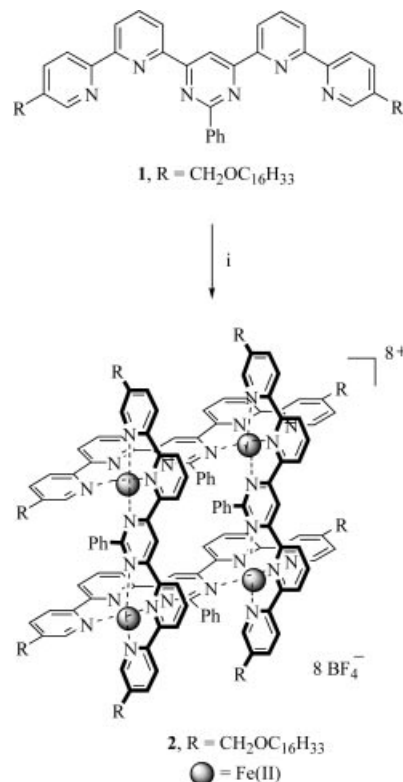
Synthesis of Ligand **1** and Self-Assembly of $[2 \times 2]$ -Grid-Type Fe^{II} Complex **2**

The synthesis of the long-chain-substituted ligand **1** is outlined in Scheme 1. Deprotonation of 2-bromo-5-(hydroxymethyl)pyridine (**3**), which was readily accessible from commercially available 2-hydroxy-5-pyridinecarboxylic acid,^[14] with sodium hydride in DMF followed by treatment with hexadecyl iodide afforded ether **4** in 66% yield. Stannylation of **4** with a hexamethyldistannane/ $\text{Pd}(\text{PPh}_3)_4$ system in refluxing toluene produced **5**, which was in turn coupled with 2,6-dibromopyridine in the presence of $\text{Pd}(\text{PPh}_3)_4$ to afford bipyridine derivative **6** in 52% yield. Twofold Stille coupling of 4,6-dichloro-2-phenylpyrimidine^[15] with 2 equiv. of **7**, which was prepared by stannylation of **6** with a hexamethyldistannane/ $\text{Pd}(\text{PPh}_3)_4$ system, in refluxing toluene in the presence of $\text{Pd}(\text{PPh}_3)_4$ gave the desired ligand **1** in 57% yield.



Scheme 1. Synthesis of ligand **1**, i) NaH, DMF, then $\text{C}_{16}\text{H}_{33}\text{I}$; ii) $\text{Me}_3\text{SnSnMe}_3$, $\text{Pd}(\text{PPh}_3)_4$, toluene; iii) 2,6-dibromopyridine, $\text{Pd}(\text{PPh}_3)_4$; iv) $\text{Me}_3\text{SnSnMe}_3$, $\text{Pd}(\text{PPh}_3)_4$, toluene; v) 4,6-dichloro-2-phenylpyrimidine, $\text{Pd}(\text{PPh}_3)_4$.

Reaction of **1** with $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile/chloroform (1:1) proceeded smoothly and cleanly to yield the corresponding $[2 \times 2]$ -grid-type complex **2** in quantitative yield, as similarly shown earlier for the formation of related complexes (Scheme 2).^[2–4] The electrospray mass spectrum of **2** confirms its $[2 \times 2]$ -grid-like structure in solution.^[16]



Scheme 2. Formation of the $[2 \times 2]$ -grid-type Fe^{II} complex **2**, i) $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{CHCl}_3/\text{CH}_3\text{CN}$ (1:1).

STM Investigation of Ligand **1** Adsorbed on HOPG

Self-assembly of ligand **1** on HOPG results in a highly ordered structure; the representative STM image of **1** is shown in Figure 1. Brighter and darker lamellae alternate within the image, where a bright color represents higher electron density. The periodicity of the lamellae is 55 Å. The brighter moiety exhibits a width of 25 Å and the darker moiety a width of 30 Å. The bright stripe shows a structured pattern with numerous small bright spots and is attributed to the aromatic rings. The darker stripe presents

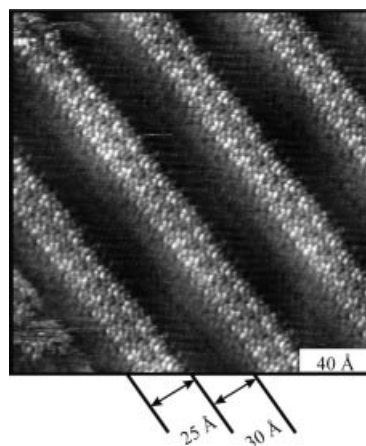
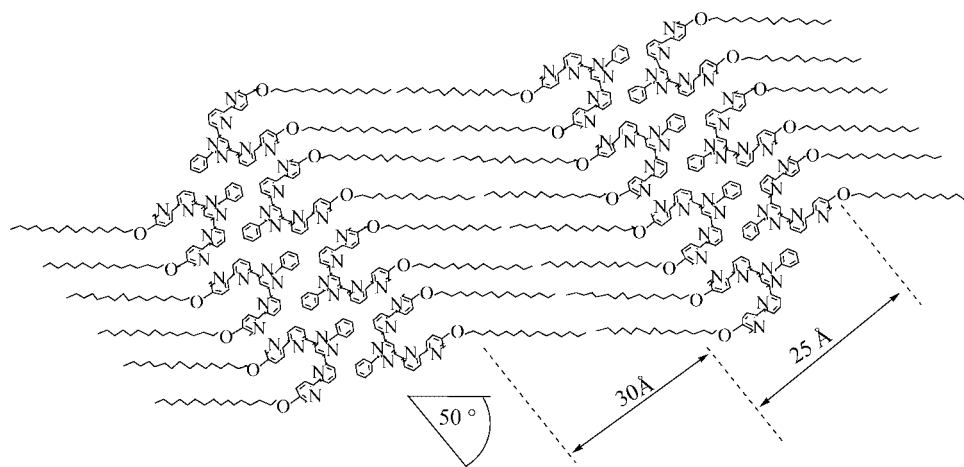


Figure 1. STM image of **1** on HOPG from 1,2,4-trichlorobenzene: Lamellar widths: 25 and 30 Å; $V_{\text{bias}} = -362$ mV, $I_{\text{set}} = 23.8$ pA.



Scheme 3. Proposed model for the conformation and ordering of **1** on graphite.

an additional pattern of linear arrays of spots, which form an angle of 50° with the ribbons. These linear arrays are assigned to the alkyl chains in **1**. The image can be interpreted as a flat arrangement of the aromatic rings on the surface, which is expected for optimal contact between the monolayer and the basal plane of graphite. The alkyl chains in **1** are ordered commensurately with the graphite lattice.^[13] The conformation of the aromatic units of **1** on the surface would be analogous to those observed for related compounds both in solution and in the solid state, i.e., a *transoid* conformation of the NC–CN bonds connecting the heterocycles, as indicated in our previous studies.^[11,17–19] In the lower left corner of the STM image (Figure 1<yigr1>) a defect can be observed.

A plausible model for the arrangement of **1** on the surface is shown in Scheme 3. In this model, the bright stripes are formed by the aromatic part of two rows of molecules of **1**, which may be stabilized by weak intramolecular C–H...N interactions.^[11,17–19] The alkyl chains form an angle of 50° with this stripe. From geometrical estimations the expected widths of the ribbons fit very well with the experimental values. The tilt angle of the alkyl chains with the main axis of the lamellae allows the optimal contact of ca. 4.5 Å between neighboring chains.^[11] The comparison of the length of the alkyl chains in **1** and the observed width of the darker stripes in the image suggests a noninterdigitated assembly of the alkyl chains.

STM Investigation of [2 × 2]-Grid-Type Fe^{II} Complex **2** Assembled on HOPG

Representative STM images of the [2 × 2]-grid-type Fe^{II} complex **2** on HOPG are shown in Figure 2. The large scan area exhibits two domains of alternating brighter and darker ribbons (Figure 2a). On the first glimpse both domains seem to represent the same structure with changing preferred directions. A closer look reveals that the periodicities of the ribbons differ between 42 Å (domain A) and 23 Å (domain B), respectively, but both domains can be eas-

ily distinguished from the features of ligand **1** (Figure 1). Hence, we assume that **2** forms at the solution/HOPG interface at least two different morphologies. The formation of (pseudo)polymorphs^[20] in 2D monolayers – sometimes depending on the solvent^[21] – is known but the grid-like complexes of HOPG polymorphism were only observed in the case of different substituents in the periphery and in the center of the complexes, respectively.^[10]

A detailed view of domain A (Figure 2b) shows that the brighter stripes are built from square-like entities with an edge length of 22 to 24 Å whereas the darker ribbons are structured by more narrow and broader stripes perpendicular to the ribbon direction. Because of the differences in electron density we attribute the brighter ribbons to the grid-like structure of the aromatic part of **2** and the darker bands to the alkyl substituents.

Regarding a reasonable model for the arrangement of **2** in domain A the fourfold symmetry of the square-like entities in Figure 2b gives hints for an arrangement of **2** with the *C*₄ axis perpendicular to the substrate surface (Scheme 4c). In Scheme 4a the geometrical dimensions of the grid core of **2** show that we expect an edge length for the squares without the alkyl chains of 18 Å. The larger size of the square-like shapes in Figure 2b suggests that each grid-like complex is rotated along the *C*₄ axis so that the ligands are no longer parallel and orthogonal, respectively, to the main direction of the bright stripes but form an angle of 20–30° and 110–120°, respectively (Scheme 4c). A further stripy fine structure of the square-like bright areas in the direction of one set of two parallel ligands per complex molecule with the above given angles supports this assumption. There is no optimal contact possible between the alkyl chains and the graphite surface due to the nonplanar structure of **2**. We suggest that the chains adopt a conformation similar to that shown in Scheme 4b, which exhibits the side view of one ligand molecule **1** in its conformation in complex **2**. Such conformation allows close contact between a part of an alkyl chain and graphite. The width of the darker ribbons of 18 Å is too small for a noninterdigitated arrange-

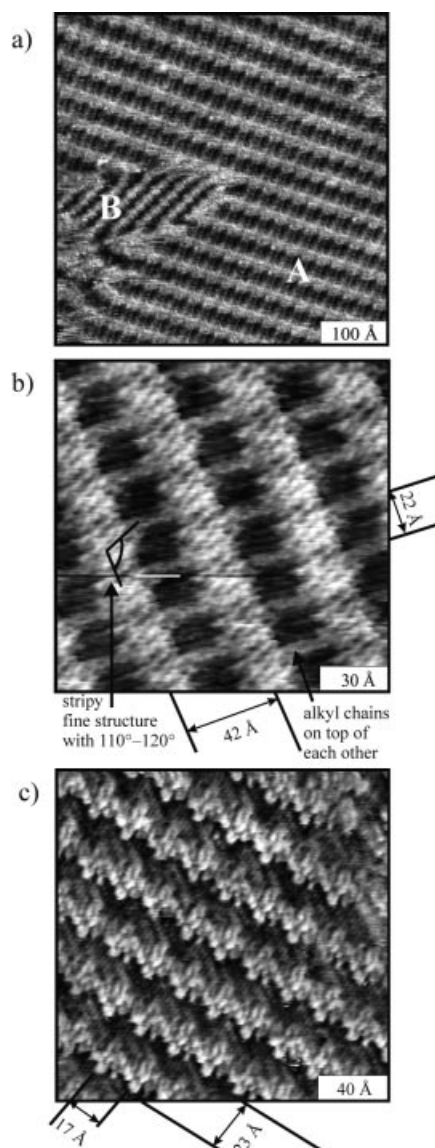
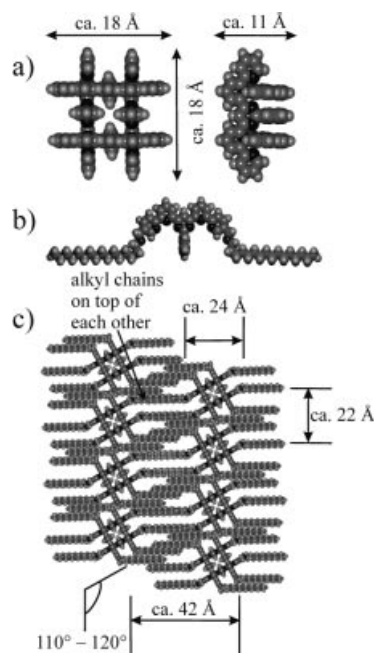


Figure 2. STM images of **2** on HOPG from 1,2,4-trichlorobenzene: Large-scan-area image with two different domains A and B ($V_{\text{bias}} = -651$ mV, $I_{\text{set}} = 39.4$ pA) (a), detailed view of domain A with a lamellar structure (periodicity: 42 Å) and a periodic fine structure within each lamella (periodicity: 22 Å), a stripy fine structure with an angle of ca. 115° with respect to the lamella axis is visible, too ($V_{\text{bias}} = -410$ mV, $I_{\text{set}} = 36.6$ pA) (b), detailed view of domain B with a lamellar structure (periodicity: 23 Å) and a periodic fine structure within each lamella (periodicity: 17 Å; $V_{\text{bias}} = -344$ mV, $I_{\text{set}} = 44.1$ pA) (c).

ment of the alkyl chains despite the above suggested conformation. Hence, we assume interdigitation which on the other side would lead, with the assumed orientation of the grid-like complexes, to a partial bumping of the alkyl chains (see Scheme 4c). Though the resolution of the STM image in Figure 2b does not give enough information on the exact ordering of the alkyl chains we suppose that at these positions the alkyl chains are approximately on top of each other. This might cause the contrast of brighter stripes within the darker ribbons in Figure 2b because of the topography and not primarily due to higher electron density.

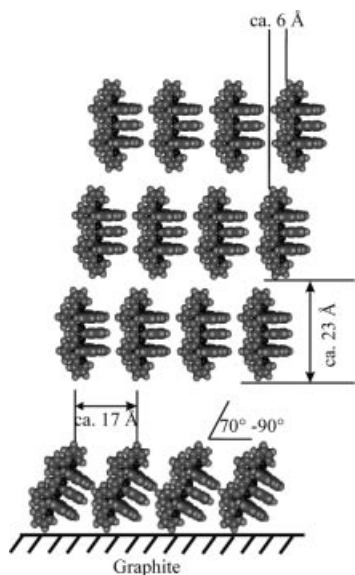


Scheme 4. Proposed model for the arrangement of **2** on HOPG in domain A: top view of one grid-like complex along the C_2 axis (a, left), side view of one grid-like complex (a, right), side view of one ligand **1** with the proposed conformation of the alkyl chains ensuring close contact between the surface and the alkyl chains (b), top view of the arrangement of the grid-like complexes on HOPG (c).

A detailed view of domain B shows lamellae which are built from a bright and a dark band, the dark formed by fine stripes with an angle of 40° with respect to the ribbons (Figure 2c). These stripes are assigned to the alkyl chains. The bright parts are attributed to the high electron density aromatic moieties of complex **2** showing an additional fine structure with a periodicity of 17 Å.

Comparing with the much larger periodicity of the ribbons in domain A (42 Å, Figure 2b), we suggest an edge-on arrangement of the complexes on the graphite in domain B (periodicity 23 Å, Figure 2c), though we cannot assign unambiguously the fine structure of the bright parts to the structure of the grid-like complex. The edge-on arrangement of the complexes on the graphite may be accompanied by a tilt angle of up to 70° which would lead to a projected area of 17×18 Å (Scheme 5). This arrangement should lead to an improved contact between the two alkyl chains next to the graphite and the graphite surface at the expense of the other six alkyl chains which are bent to come at least partially into contact with the graphite surface. An additional consequence of such an arrangement is a stacking of the complexes which should be advantageous due to their highly charged character. Within one ribbon the complexes are assumed to be parallel to each other. Comparing adjacent ribbons a shift between two neighboring molecules of ca. 6 Å can be found which might be caused by the packing of the alkyl chains.

The two arrangements of complex **2** coexist on HOPG (see Figure 2a) but we do not yet know how the formation of one or the other morphology can be controlled. The



Scheme 5. Proposed model for the arrangement of **2** on HOPG in domain B: top view of the arrangement of the grid-like complexes (top), side view of the arrangement of the grid-like complexes parallel to the graphite surface with an angle of 70° resulting in a projected area of 17×18 Å (bottom). Only the grid cores are shown, the alkyl chains are omitted for clarity.

forms are stable enough not to be transformed into each other by the STM tip or any other external trigger present in the course of our STM experiments.

Conclusions

The doubly functionalized ligand **1**, having CH₂OC₁₆H₃₃ moieties at the terminal pyridine rings, was designed as a new bis(tridentate) ligand and synthesized. Treatment of **1** with Fe(BF₄)₂·6H₂O in CHCl₃/CH₃CN led to the spontaneous formation of a [2×2]-grid-type Fe^{II} complex **2** in a quantitative yield. The STM investigations of both ligand **1** and the Fe^{II} complex **2** on graphite revealed their stable, regular arrangements on the surfaces. Complex **2** shows two different morphologies – a flat and an edge-on assembly of the grid-like complexes on HOPG. We do not yet know the factors determining the formation of one or the other arrangement. Importantly, stability of the monolayers of the long-chain-substituted complex **2**, and thus, reproducibility of their STM images have been significantly enhanced compared to the corresponding unsubstituted complex. Therefore, the present results suggest that the introduction of long alkyl chains into the ligand would be a useful strategy for the STM investigations of the related grid-type complexes as well as other metallo-supramolecular architectures on HOPG surfaces.

Experimental Section

General: Melting points were measured with a digital Electrotherma apparatus and are uncorrected. ¹H NMR spectra were recorded with a Bruker AC200 spectrometer in CDCl₃ at 200 MHz

under ambient conditions; chemical shifts are given in ppm using TMS as reference. ¹³C NMR spectra were recorded with a Bruker AC200 spectrometer in CDCl₃ at 50 MHz, also under ambient conditions; chemical shifts are given in ppm using the solvent peak as reference. Fast atom bombardment (FAB) mass spectra were recorded with a ZAB-HF VG spectrometer with *m*-nitrobenzyl alcohol as the matrix. Electrospray (ES) mass spectra were recorded with a triple quadrupole mass spectrometer Quattro II. The microanalyses were carried out at the Service Central de Microanalyse du CNRS, Faculté de Chimie, Strasbourg. Column chromatography was carried out on Merck silica gel 60 or Merck alumina activity II–III. 2-Bromo-5-(hydroxymethyl)pyridine (**3**)^[14] and 4,6-dichloro-2-phenylpyrimidine^[15] were prepared according to known procedures.

2-Bromo-5-(hexadecyloxymethyl)pyridine (4): To a suspension of sodium hydride (128 mg, 5.32 mmol, 60% dispersion in oil) in anhydrous DMF (6 mL) was added 2-bromo-5-(hydroxymethyl)pyridine (**3**)^[14] (500 mg, 2.7 mmol) and the reaction mixture was stirred at room temperature for 1 h. The suspension was cooled to 0 °C and hexadecyl iodide (1.06 g, 3.0 mmol) was added to it. The mixture was then allowed to warm to room temperature and stirred for 44 h. After evaporation of the solvent, the residue was subjected to chromatography on silica gel eluting with hexane/EtOAc (4:1, v/v) to afford **4** as a colorless powder (723 mg, 66%). M.p. 47 °C. ¹H NMR (200 MHz, CDCl₃): δ = 0.84 (t, *J* = 6.7 Hz, 3 H, CH₃), 1.22 (m, 26 H, CH₂), 1.57 (quint, *J* = 6.7 Hz, 2 H, OCH₂CH₂), 3.44 (t, *J* = 6.4 Hz, 2 H, OCH₂), 4.42 (s, 2 H, C_{py}CH₂O), 7.41 (d, *J* = 8.2 Hz, 1 H, 4-H), 7.51 (dd, *J* = 8.2 and 2.4 Hz, 1 H, 3-H), 8.28 (d, *J* = 1.8 Hz, 1 H, 6-H). ¹³C NMR (50 MHz, CDCl₃): δ = 14.0, 22.6, 26.1, 29.3, 29.4, 29.6, 31.9, 69.4, 71.0, 127.8, 133.5, 137.8, 141.1, 149.2. MS (FAB): *m/z* (%) = 412.1 (100) [M + H]⁺. IR (KBr): ν̄ = 2954, 2916, 2851, 1586, 1566, 1473, 1458, 1388, 1110, 1089, 1026, 842, 824, 716, 630 cm⁻¹. C₂₂H₃₈BrNO (412.46): calcd. C 64.20, H 9.31, N 3.41; found C 64.07, H 9.46, N 3.38.

2-Bromo-6-[5'-(hexadecyloxymethyl)pyrid-2'-yl]pyridine (6): A mixture of **4** (1 g, 2.42 mmol), hexamethyldistannane (880 mg, 2.66 mmol), and Pd(PPh₃)₄ (70 mg, 0.060 mmol) in toluene (16 mL) under argon was refluxed for 4 h. 2,6-Dibromopyridine (1.26 g, 5.32 mmol) and Pd(PPh₃)₄ (120 mg, 0.11 mmol) were added to the mixture and the reaction mixture was further refluxed under argon for 20 h. After evaporation of the solvent, the residue was subjected to chromatography on silica gel eluting with hexane/EtOAc (9:1, v/v) to afford **6** as a colorless powder (620 mg, 52%). M.p. 67 °C. ¹H NMR (200 MHz, CDCl₃): δ = 0.88 (t, *J* = 6.1 Hz, 3 H, CH₃), 1.25 (m, 26 H, CH₂), 1.56–1.72 (m, 2 H, OCH₂CH₂), 3.50 (t, *J* = 6.4 Hz, 2 H, OCH₂), 4.57 (s, 2 H, C_{py}CH₂O), 7.47 (dd, *J* = 7.9 and 1.2 Hz, 1 H, 3'- or 5'-H), 7.65 (t, *J* = 7.9 Hz, 1 H, 4'-H), 7.79 (dd, *J* = 8.2 and 2.4 Hz, 1 H, 3-H), 8.37 (dd, *J* = 7.6 and 0.9 Hz, 1 H, 3'- or 5'-H), 8.38 (d, *J* = 8.2 Hz, 1 H, 4-H), 8.62 (d, *J* = 2.1 Hz, 1 H, 6-H). ¹³C NMR (50 MHz, CDCl₃): δ = 14.0, 22.6, 26.1, 29.3, 29.4, 29.6, 31.8, 70.0, 70.8, 119.5, 120.9, 127.7, 134.7, 136.0, 139.0, 141.4, 148.3, 153.6, 157.1. MS (FAB): *m/z* (%) = 489.4 (100) [M + H]⁺. IR (KBr): ν̄ = 2953, 2916, 2849, 1600, 1570, 1545, 1470, 1434, 1387, 1124, 1026, 988, 801, 777, 754, 718, 672 cm⁻¹. C₂₇H₄₁BrN₂O (489.54): calcd. C 66.25, H 8.44, N 5.72; found C 66.17, H 8.32, N 5.74.

4,6-Bis{6'-[5'-(hexadecyloxymethyl)pyrid-2'-yl]pyrid-2'-yl}-2-phenylpyrimidine (1): A mixture of **6** (300 mg, 0.61 mmol), hexamethyldistannane (221 mg, 0.64 mmol), and Pd(PPh₃)₄ (21 mg, 0.018 mmol) in toluene (4 mL) under argon was refluxed for 25 min. After evaporation of the solvent, the resultant crude stannylated product **7** was used for the following coupling reaction

without further purification. ^1H NMR (200 MHz, CDCl_3): δ = 0.39 [s, 9 H, $\text{Sn}(\text{CH}_3)_3$], 0.89 (t, J = 6.1 Hz, 3 H, CH_3), 1.26 (m, 26 H, CH_2), 1.63 (quint, J = 6.7 Hz, 2 H, OCH_2CH_2), 3.50 (t, J = 6.4 Hz, 2 H, OCH_2), 4.57 (s, 2 H, $\text{C}_{\text{py}}\text{CH}_2\text{O}$), 7.44 (dd, J = 7.3 and 1.5 Hz, 1 H, 3'- or 5'-H), 7.64 (t, J = 7.3 Hz, 1 H, 4'-H), 7.80 (dd, J = 8.2 and 2.4 Hz, 1 H, 3-H), 8.27 (dd, J = 7.9 and 1.2 Hz, 1 H, 3'- or 5'-H), 8.54 (d, J = 7.9 Hz, 1 H, 4-H), 8.62 (d, J = 1.5 Hz, 1 H, 6-H). A mixture of **7** (334 mg, 0.58 mmol), 4,6-dichloro-2-phenylpyrimidine (**8**)^[15] (66 mg, 0.29 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (34 mg, 0.029 mmol) in toluene (5 mL) under argon was refluxed for 21 h. After evaporation of the solvent, the residue was taken up in CHCl_3 and filtered through a short pad of alumina. The solvent was evaporated, the residue was taken up in MeOH/acetone (1:1, v/v), and the precipitate formed was centrifuged off, washed with MeOH/acetone and dried in vacuo. The crude product thus obtained was further purified by column chromatography on alumina eluting with hexane/ CHCl_3 (1:1, v/v) to afford **1** as a colorless powder (162 mg, 57%). M.p. 141 °C. ^1H NMR (200 MHz, CDCl_3): δ = 0.87 (t, J = 5.8 Hz, 6 H, CH_3), 1.24 (m, 52 H, CH_2), 1.67 (quint, J = 7.0 Hz, 4 H, OCH_2CH_2), 3.56 (t, J = 6.4 Hz, 4 H, OCH_2), 4.64 (s, 4 H, $\text{C}_{\text{py}}\text{CH}_2\text{O}$), 7.56–7.65 (m, 3 H, *m*- and *p*-H), 7.87 (d, J = 6.7 Hz, 2 H, 3'- or 5'-H), 8.05 (t, J = 7.9 Hz, 2 H, 4'-H), 8.60 (d, J = 7.9 Hz, 2 H, 3'- or 5'-H), 8.71–8.80 (m, 8 H, *o*-, 3'-, 4'- and 6''-H), 9.62 (s, 1 H, 5-H). ^{13}C NMR (50 MHz, CDCl_3): δ = 14.1, 22.7, 26.2, 29.3, 29.5, 29.6, 29.6, 29.6, 29.7, 29.8, 31.9, 70.3, 70.9, 111.5, 120.8, 121.7, 122.4, 128.4, 128.4, 130.6, 134.4, 136.0, 137.9, 137.9, 148.5, 153.8, 155.3, 155.4, 163.9, 164.1. MS (FAB): m/z (%) = 973.7 (100) [$\text{M} + \text{H}$]⁺. IR (KBr): $\tilde{\nu}$ = 3060, 2918, 2850, 1720, 1556, 1540, 1471, 1377, 1263, 1115, 1022, 994, 814, 50, 718, 690, 652, 634 cm^{-1} . HR-MS (FAB): $\text{C}_{64}\text{H}_{89}\text{N}_6\text{O}_2$ (1022.51): calcd. m/z = 973.704702, found m/z = 973.705754 [$\text{M} + \text{H}$]⁺.

[2×2]-Grid-Type Fe^{II} Complex (2): A mixture of **1** (5 mg, 5.14 μmol) and $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.73 mg, 5.14 μmol) in CHCl_3 (0.4 mL) and CH_3CN (0.4 mL) under argon was refluxed. The reaction was monitored by ^1H NMR spectroscopy and ES mass spectrometry and was proven to be completed after 15 h. Evaporation of the solvents afforded pure complex **2** in a quantitative yield as a dark green powder. ^1H NMR (200 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$): δ = -17.8, -10.2, 0.0, 2.3, 2.8, 5.6, 7.3, 13.4, 14.2, 17.5, 55.5, 60.0, 66.4, 74.5. MS (ESI): m/z = 2318.7 [$\text{M} - 2 \text{BF}_4$]²⁺, 1517.0 [$\text{M} - 3 \text{BF}_4$]³⁺, 1116.4 [$\text{M} - 4 \text{BF}_4$]⁴⁺, 876.3 [$\text{M} - 5 \text{BF}_4$]⁵⁺.

STM Investigations: STM measurements were carried out under ambient conditions with a low-current RHK 1000 control system. STM imaging of the adlayers was performed at the internal interface between HOPG and a concentrated solution of the ligand **1**, dissolved in 1,2,4-trichlorobenzene, according to the procedure of Rabe.^[13a] A drop of the solution was placed on a freshly cleaved HOPG surface, while the surface had already been scanned by STM under the 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 $\mu\text{m s}^{-1}$. 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. Complex **2** was dissolved in acetonitrile at a concentration less than 1 wt.-%. A drop 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 next to the sample). Then the sample was taken out of the Petri dish and dried fully under ambient conditions. The molecular structure of the adlayer was probed by STM under air. The distances and angles were determined by using an internal calibration. The overall error of

these determinations is estimated below $\pm 5\%$ for distances and angles.

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