The organometallic 'Molecular Tinkertoy' approach to planar grid polymers

Thomas F. Magnera, Laurence M. Peslherbe, Eva Körblová, Josef Michl *

Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA

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Abstract

A general approach is outlined for the synthesis of thin-layer materials of arbitrarily configured structure ('designer solids'), based on confinement to two dimensions. The synthesis of a building module, the tetra-n-butylammonium salt of lanthanum(III)bis[5,10,15,20-tetrakis(4-pyridyl)porphyrinate] (1), is described. It is shown by grazing incidence IR spectroscopy that this cross-shaped molecule adheres firmly to a mercury surface, with the porphyrin rings parallel to the surface and the pyridine rings carried by the upper porphyrin ring ready for linear coupling. The proposed surface-confined synthesis of a square grid, which would define a first layer of a designer solid, can now be tested. © 1997 Elsevier Science S.A.

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1. Introduction

Organometallic sandwich compounds appear to be ideal building blocks in the quest (e.g. [1–3]) for ultrathin two-dimensionally 'infinite' planar grid polymers, whose synthesis represents the first step in our effort to use molecular construction kit chemistry to prepare thin layers of designer solids [2,4–7]. We survey the present status of the project and report the synthesis of a promising building module, the La(III) complex of 5,10,15,20-tetra(4-pyridyl)porphyrin (1).

2. Molecular construction kits

2.1. Modular chemistry

The synthesis of macromolecules and molecular assemblies from repetitive modules and investigation of their properties is a vast area of endeavour. It encompasses both supramolecular [8] and giant-single-molecule [9] chemistry, and its targets range from linear polymers, planar polymers, dendrimers, and porous crystals to nanotubes, catenanes, helicates, molecular boxes and cubes, self-assembled monolayers, cluster assemblies, and numerous others. Many aspects of modular chemistry are touched upon in a book that is about to appear [10].

2.2. Designer solids

We wish to synthesize sturdy thin layers of designer solids with structure periodic in the two large dimensions and arbitrarily aperiodic in the thin dimension, and with suitably located 'active' groups if desired [2,4–7]. We need general synthetic procedures that permit a free choice of prespecified locations, orientation, and nature of the active groups. These could be light absorbers or emitters, electron donors or acceptors, charged or magnetic groups, non-linear optical chromophores, complexing or reactive groups, etc. They could be held rigidly, could swing or rotate, and are to be carried by a rigid-rod scaffolding whose dimensions dictate the degree of porosity and the distances between the active elements. Such scaffolding would offer a support of choice for many molecular electronic devices that have been proposed [11].

The basic elements of the scaffolding are molecular rods and 3-, 4-, or 6-fold connectors. The rod dimensions are to be molecular, up to ~ 1 nm in diameter and up to ~ 5 nm in length, and they are to be attached to the connectors by strong bonds, preferably covalent, such that the whole thin layer is a single giant molecule.

* Corresponding author. Tel.: + 1 (303) 492-6531; fax: + 1 (303) 492-5894.

Thus, the chemistry involved is not of the supramolecular, but of the single-giant-molecule variety. Because of the analogy to children's toy construction sets, we refer to it as the chemistry of 'Tinkertoy-like' [12] construction kits.

2.3. Surface-anchored and free-floating structures

In addition to surface-anchored objects, such as our synthetic target, molecular construction kits can also be used to synthesize free-floating objects (much progress has been made by others, e.g. [13–19]) and porous crystals (for a brief survey see [20]). Our decision to concentrate on surface-anchored objects was motivated by the challenge of synthesis constrained to two dimensions, dealing with ng quantities of materials without access to many of the usual analytical tools, and by the novelty of handling macroscopic objects that are only a few Å thick. We were fascinated by the potential utility of these synthetic targets. For example, a bare grid or scaffolding, without any active groups, could be used for ultrafast size-based molecular separations and for the production of regular arrays of quantum dots smaller than those available by photolithography. Even an irregular grid might be useful for separations if deposited on a fine metal mesh or a perforated polymer-based or ceramic membrane, or imbedded in a permeable polymer membrane, provided that cracks between domains and defects in them could be sealed.

2.4. Planar grid polymers as the starting point

Our plan has been to start with the synthesis of the ground floor, i.e., a covalent two-dimensional molecular grid. Then, we hope to erect a regular set of vertical rods or couplers at strategic locations in the grid and to proceed with the covalent construction of the second floor. This could be quite different chemically, provided that its dimensions matched. A third floor would follow, perhaps erected on rods of a different length, etc. The process of building a multilayer structure would thus resemble linear polymer synthesis on a solid support and could, in principle, be similarly automated. The difference between our planned and the currently known covalent multilayers [21,22] is primarily due to the rigidity of the elements of the construction kit, which should permit the synthesis of arbitrarily porous structures.

2.5. Molecular rods

Our initial efforts concentrated on the synthesis of elementary building blocks. The first were rigid-rod molecules with axial terminal substituents. Some were known at the outset, such as derivatives of polyphenyls and polyacetylenes. Due to efforts in several laborato-

ries, many are known presently (oligomers of [1.1.1]propellane, dubbed 'staffanes' [4–6,23,24], formal oligomers of [2.2.2]propellane, dubbed 'molecular rods' [25], polycubyls [26,27], oligomeric 10-vertex [28] and 12-vertex [28,29] p-carboranes, dubbed 'carborods', and various multicomponent rods (e.g. [30])). This provides a variety of rod lengths, easily specified to the nearest Å. Additional development is needed, particularly of electrically conducting rods, which would permit the imposition of defined electrical potentials at chosen scaffolding floors.

2.6. Molecular connectors

Our current efforts are directed at the synthesis of molecular connectors and the development of control techniques for directed synthesis of low-dimensional covalent objects, avoiding the formation of three-dimensionally cross-linked polymers that tend to form spontaneously. We have chosen to build the control elements into the structure of the connector, but it would be equally possible to build them into the structure of the rods.

We envisage two kinds of connectors, 'star' and 'point' [2]. A star connector contains a center carrying 3, 4, or 6 rigid arms ('half-rods') in a plane (e.g. hexaethynylbenzene). The functionalities at the arms ends permit mutual linear coupling through the termini. As an alternative, the linear coupling could occur to a rod terminus, and more complex schemes can be envisaged. Most obvious central units for star connectors are a benzene or cyclobutadiene ring. Point connectors are bare central units with 3, 4, or 6 reactive sites (e.g. transition metals), capable of attaching rigid rod termini at regular angles in a plane, and perhaps others axially. Although many known molecules appear potentially useful as connectors, most have little value for us until they are elaborated to provide a control element for two-dimensional construction.

3. Control of two-dimensional synthesis

3.1. The control elements

The way that we have chosen to assure that the polymerization of our connectors can proceed in only two dimensions is to confine them physically to a surface, as was done before in ordinary one-dimensional polymerization reactions of molecules tethered to a surface [31]. In our case, the nature of the constraint should be such as to assure simultaneously that the connectors are oriented properly for the intended two-dimensional coupling reaction.

The confinement is to be accomplished by mounting the connectors on flat pedestals fitted with three or more

tentacles that carry functional groups with a high affinity for the surface [2,7]. In this way, the connector is prevented from leaving the surface and is oriented with the rigid rods parallel to the surface. Metal sandwich complexes are a natural initial choice, with one deck acting as the connector proper, the metal acting as a mounting pillar, and the other deck serving as the platform to which the tentacles are attached. However, in later stages, when we shall be concerned with optimizing the conditions for the attachment of further floors, other choices may be preferable, in order to direct the rods partially away from the surface.

Three cases can be distinguished. (i) Symmetrical sandwich complexes are easy to prepare, but their use requires that the tentacles be identical with the arms of the star connector. The pyridine rings of 1 are an example. As shown below, the 4 pyridines at the bottom deck assure adhesion to a surface, and the 4 at the top deck are available for coupling. (ii) Intrinsically asymmetrical sandwich complexes, such as cyclobutadienecobaltcyclopentadienyl derivatives [32], with very different reactivities in the two decks, also available easily, permit facile differential functionalization of the bottom deck with tentacles. (iii) Differentially functionalized, but intrinsically symmetric sandwich complexes appear the hardest to synthesize.

After coupling into a grid, the tentacles can be either severed and discarded, permitting an easy removal of the product grid from the surface (single-ply grid), or they can be deactivated into a form that permits lifting from the surface, and then themselves coupled into a second grid layer (two-ply grid). The latter is easiest in the above case (i), with which we shall deal presently.

3.2. The coupling reaction

The requirements imposed on the coupling reaction are severe. First, it must not interfere with the firm adhesion of the tentacles to the surface. Second, the building elements must be chosen so as to make all irregularities and defects left after the coupling process unfavorable in terms of free energy, e.g. by causing high strain. Rigid building elements and rigid angular requirements in the coupling reaction are clearly advantageous. However, low free energy of the perfect grid will only help to minimize the number of defects and maximize the size of regular domains if the coupling is performed under equilibrium conditions, or if subsequent bond-breaking and bond-remaking events permit annealing into regular two-dimensional structure. The coupling must therefore be reversible, yet the primary condition on the grid is that it must be sturdy and its bonds not easily broken: the coupling must be both reversible and irreversible.

We plan to meet these contradictory conditions in two ways. One is to choose a coupling reaction that is

reversible only under conditions unlikely to be encountered during the use of the grid. The other is to form the grid with a 'phantom coupler', which couples reversibly by kinetically labile weak bonds, anneal it, and subsequently take advantage of the accessibility of all sites to replace the phantom by the real irreversibly binding coupler.

3.3. The 2-D confinement

The requirements imposed on the tentacles and the confining surface are also severe. The first is compatibility with the coupling reaction: the adhesion of the tentacles to the surface must survive all conditions encountered during the coupling and annealing, since even the departure of a minute fraction of the molecules into the third dimension might introduce disastrous three-dimensional cross-linking. Second, to minimize defects, the surface should be easily cleaned and kept clean, and it must be atomically flat over a macroscopic area. Third, the adhesion must not interfere with free translation and rotation of the connectors on the surface, permitting them to assume the positions and orientation appropriate for the target grid.

The structure of some crystal surfaces may match the geometry of the desired grid within the tolerances required by the rigidity of the molecular rods. However, their use is not a satisfactory option if the synthetic procedure is to be general and offer an arbitrary choice of the size of the hexagons, squares, or triangles in the grid to within 1 Å. Thus, the adsorption of the tentacles to the surface atoms needs to be vertically strong and laterally weak. Although some macroscopically flat solid surfaces may meet this condition, particularly at elevated temperatures, we have chosen to work with a liquid surface, which is atomically flat and will not impose any inherent lateral periodic structure of its own. A liquid also permits easy adjustment of surface concentration and transfer of adsorbates to other substrates by Langmuir–Blodgett techniques [33].

For initial simplicity, we have chosen mercury as the liquid on which the tentacles are to adsorb, even though it is likely that a polar/non-polar liquid interface will ultimately prove superior for health and safety reasons. The surface of mercury is easily cleaned and kept clean, and Langmuir–Blodgett work on it has been reported [34]. The very low solubility of all likely components of the construction kit in mercury should define the vertical position of the adsorbed mounted pedestals to within a fraction of an Å relative to the neighbors, helping to line up the reacting connectors optimally. This is particularly important in cases such as 1, with tentacles of the lower deck and arms of the upper deck identical, where there is danger of coupling a lower deck of one monomer to an upper deck of another if their vertical positions are not well defined.
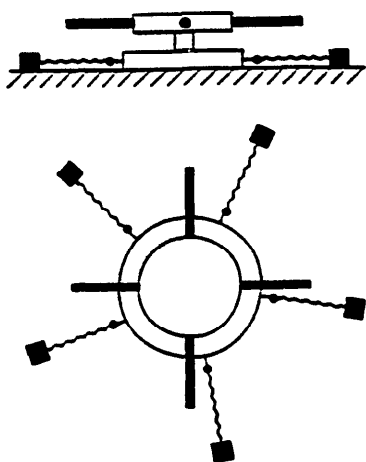
Fig. 1. Symbolic representation of a general pedestal-mounted star connector.

A fair amount is known about adsorption on mercury, particularly from polar solutions. Metallic conductivity permits easy electrochemical monitoring of surface concentrations and chemical changes, and offers some control of adsorption by imposition of a well-defined surface potential. Many metal ions can be introduced as amalgam. Metallic reflectivity permits monitoring of the coupling process by grazing incidence IR and Raman spectroscopy.

3.4. The synthetic target

Fig. 1 shows a complete pedestal-mounted and tentacled connector. The synthetic challenge is different than usual, since the target is a set of functions rather than a particular chemical structure. The detailed chemical nature of the decks and of the metal joining them is immaterial, as is the nature of the arms on the upper and the tentacles on the lower deck, as long as they are stable and perform their functions. The only structural factors that are essential are the number and the length of the arms and the length of the coupler, and these need to be chosen carefully in order to control the grid cell dimensions. At the moment, we are merely attempting to demonstrate the feasibility of the concept, and any grid cell dimensions will do. We have selected a target that promised easy synthesis and the desired functional properties.

4. Synthesis of a lanthanum–porphyrin sandwich 1, a tetragonal pedestal-mounted connector

Like the metal complexes of cyclobutadiene, porphyrin offers an obvious central moiety for a cross-shaped star connector. Sandwich complexes of porphyrins with rare earth metals are known and quite stable [35,36], and a variety of meso-tetrasubstituted

porphyrins are commercially available. The 4-pyridyl substituent represents a natural choice for connector arms, since the pyridine nitrogen couples readily with a variety of metal atoms, and could, in principle, also be coupled by double alkylating agents. The latter type of coupling is not strictly linear, since it typically involves attachment to sp^3 hybridized carbons and thus a tetrahedral bend next to each pyridine ring, but for initial experiments with two-dimensional synthesis this might be acceptable. Pyridine is known to adsorb on metals from solutions [37], and we hoped that 1 will use the 4 pyridine substituents on one of its decks for strong adsorption on a mercury surface from other solvents as well. Clearly, this was not guaranteed, since the molecule could also use two rings from each deck, or perhaps could fail to adsorb strongly at all. The fact that only a one-step synthesis from commercial materials was required encouraged us to find out.

1
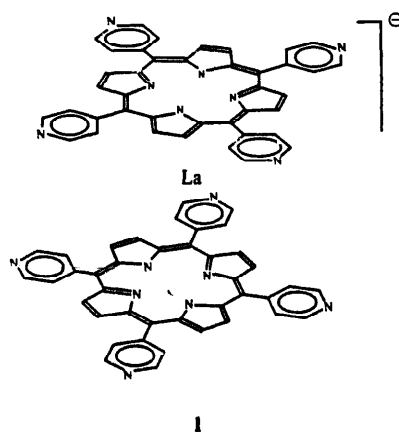
The synthesis and, particularly, the purification, turned out to be more difficult than anticipated, since the pyridine nitrogens tend to complex metal ions. The standard synthetic conditions [38–40] call for heating the free-base porphyrin with lanthanum tris(acetylacetonate) hydrate in a high-boiling solvent, such as 1,2,4-trichlorobenzene. We used the lithium salt of the porphyrin, which produced the desired product faster, after a 12-h heating. Since removal of the alkali metal ions was difficult, we converted the product (1) into its tetra-n-butylammonium salt and after purification isolated an 8% yield of spectroscopically pure tetra-n-butylammonium lanthanum(III)bis[5,10,15,20-tetrakis(4-pyridyl)porphyrinate]. It contained solvent of crystallization (1,2-dichloroethane), which also showed up in the elemental analysis, but did not disturb the surface adsorption studies. The ^{1}H-NMR spectrum of 1 in $CDCl_3$ is very similar to the known [39] spectrum of pyridinium lanthanum(III)bis(5,10,15,20-tetraphenylporphyrinate), including the characteristically broad signals of the aromatic substituents.

5. Adsorption and orientation of 1 on copper–mercury surface

5.1. Adsorption

The adsorption of the Bu_4N^+ salt of 1 onto a thin layer of mercury coated on a copper plate from a saturated (less than 10^{-4} M) solution in THF/acetic acid (30:1) under open-circuit conditions proceeded well. Grazing incidence FTIR spectrum of the mercury surface measured after thorough rinsing with the pure solvent and drying unambiguously showed the presence of the porphyrin on the surface (Fig. 2). Boiling in THF, MeOH, EtOH, t-BuOH, PhH, $PhNO_2$, 1,3-$C_6H_4Cl_2$, hexane, or water for at least 30 min did not reduce the spectral intensity, demonstrating that the adhesion is

firm. Room-temperature MeCN had no significant effect, but boiling MeCN removed the adsorbate. In contrast, the free base of 5,10,15,20-tetrakis(4-pyridyl)porphyrin adsorbs only weakly under similar conditions, is easily removed by almost any solvent, and yields no detectable IR signal for a rinsed and dried mercury surface.

5.2. Orientation

The next critical issue was, is the orientation of the adsorbed 1 correct for our purposes? The answer is contained in Fig. 2, which also shows the isotropic spectrum of $Bu_4N^+ - 1$ in a KBr pellet for comparison. Many of the absorption bands in the two spectra are the same or only slightly shifted, but certain absorption
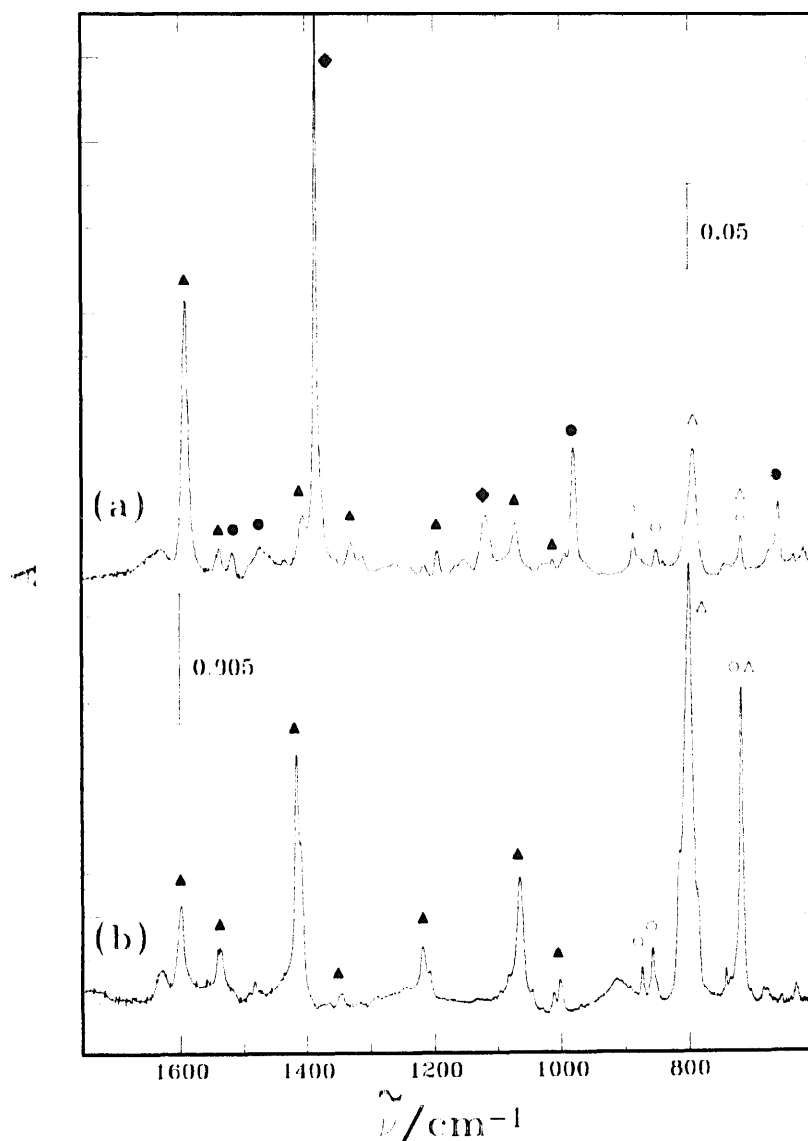

Fig. 2. IR spectra: (a) n-$Bu_4N^+ 1^-$ in KBr pellet; (b) 1 adsorbed on a mercury-coated copper plate (grazing incidence). Band assignments: ▲ △, pyridine ring modes; ●○, porphyrin ring modes (open symbols, locally out-of-plane; closed symbols, locally in-plane polarized). ◆, tetra-n-butylammonium modes.

bands present in the isotropic spectrum are clearly missing in the spectrum taken on the mercury surface. These are first, the bands due to the tetra-n-butylammonium cation, which obviously does not adhere to the surface under open-circuit conditions, and second, the bands due to in-plane polarized [41–43] vibrations of the porphyrin ring. The bands polarized perpendicular to the plane of the ring are strong, and the selection rules for molecules on a conducting surface [44] show that the porphyrin rings of the adsorbed 1 are oriented parallel to the mercury surface, as hoped. Both the in-plane and the out-of-plane polarized bands of the pyridine rings are present in the spectrum of adsorbed 1, as expected if the pyridine rings are partially twisted out of the porphyrin ring plane.

It is not known whether the presence of copper in the mercury is important for the adsorption process, but this is not a problem for our purposes, since it will always be possible to add copper intentionally if needed. Considering that the free base does not absorb firmly at all, the adsorption of 1 is surprisingly strong. The difference may be due to the presence of negative charge on 1, and it is possible that at a suitable imposed potential the free base would adsorb firmly as well. It is also conceivable that 1 forms a network on the mercury surface, with copper or mercury atoms acting as weak couplers of the pyridine tentacles in one or both decks. This could be advantageous in that it might help to preorganize the desired covalently coupled grid.

The system is now ready for an examination of various coupling reactions, and the results will be reported in due course.

6. Conclusions

The tetra(4-pyridyl)porphyrin complex 1 is accessible in a single step from commercially available materials, albeit presently in only low yield. It adsorbs firmly on mercury in the desired orientation, with the porphyrin rings parallel to the surface and the pyridine rings of the upper deck ready for linear coupling into a square grid.

7. Experimental

All reactions were performed under a dry, oxygen-free argon atmosphere. All reagents were purchased from Aldrich Chemical Company and used as received. NMR spectra of $CDCl_3$ solutions were recorded on a 300 MHz spectrometer. Chemical shifts were referenced to tetramethylsilane. The IR spectra were measured on a Nicolet Model 800 FTIR spectrometer equipped with a Harrick grazing incidence reflectance unit. The coating of copper plates by mercury was performed by cleaning

a Cu plate with chromic acid for 2 min and dipping it into mercury. The surface of the mercury was cleaned by careful aspiration under a nitrogen atmosphere.

A 250-ml three-necked flask was fitted with a condenser and an argon inlet. 5,10,15,20-Tetrakis(4-pyridyl)porphyrin (0.619 g, 1 mmol) was suspended in 1,2,4-trichlorobenzene (50 ml) and stirred under argon for about 15 min. n-BuLi (1.6 M in hexane, 2 ml, 3.2 mmol) was added via a syringe and the mixture was stirred at room temperature for 1 h. Lanthanum tris(acetylacetonate) $\cdot x H_2O$ ($x \le 2$, 1.31 g, 2.8–3.0 mmol) was added under a strong flow of argon and the mixture was refluxed for 12 h. After cooling down, tetra-n-butylammonium fluoride (1 M in THF, 0.9 ml, 0.9 mmol) was added via a syringe and the mixture was refluxed for an additional 2 h. After the reaction mixture cooled down, petroleum ether (200 ml) was added and the resulting powder was filtered off. Extraction by methanol (150 ml) gave a green solution which after evaporation of the solvent left a gray-violet powder. This powder was chromatographed on a silica gel column with a methanol/chloroform mixture (25/75). A series of precipitations successively from dichloromethane/hexane, 1,2-dichloroethane/hexane and chloroform/hexane yielded a violet powder, which was dried at 110°C under high vacuum for about 24 h to yield 58 mg (8% yield) of a crystalline powder. ^{1}H-NMR ($CDCl_3$) δ 8.8 (br s, 16 H, pyrrole), 8 (vbr s, 32 H, pyridine), 3.26 (m, 8 H, α-butyl), 2.6 (br s, ~ 11 H, $C_2H_4Cl_2$), 1.68 (m, 8 H, β-butyl), 1.47 (m, 8 H, (γ-butyl), 1.06 (t, J = 7 Hz, 12 H, δ-butyl). IR (KBr, cm^{-1}) 3016, 2959, 2925, 2874, 1635, 1590, 1539, 1517, 1473, 1381, 1118, 1071, 987, 885, 792, 718, 659. UV-vis (MeOH, nm, ϵ), 330 (27 000), 408 (198 000), 558 (6000), 608 (4800). MS (ES) m/z negative 1371 [La(TPyP)$_2^-$], positive 242 (n-Bu$_4$N$^+$). Mp > 300°C. Calcd. for $C_{96}H_{84}LaN_{17} \cdot 3$ $C_2H_4Cl_2$, C 64.09%, H 5.06%. Found: C 64.28%, H 5.15%.

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