

Hierarchical Self-Assembly of Metallo-Supramolecular Spherical Assemblies and their Characterization by NMR, ESI-FTICR, and TEM

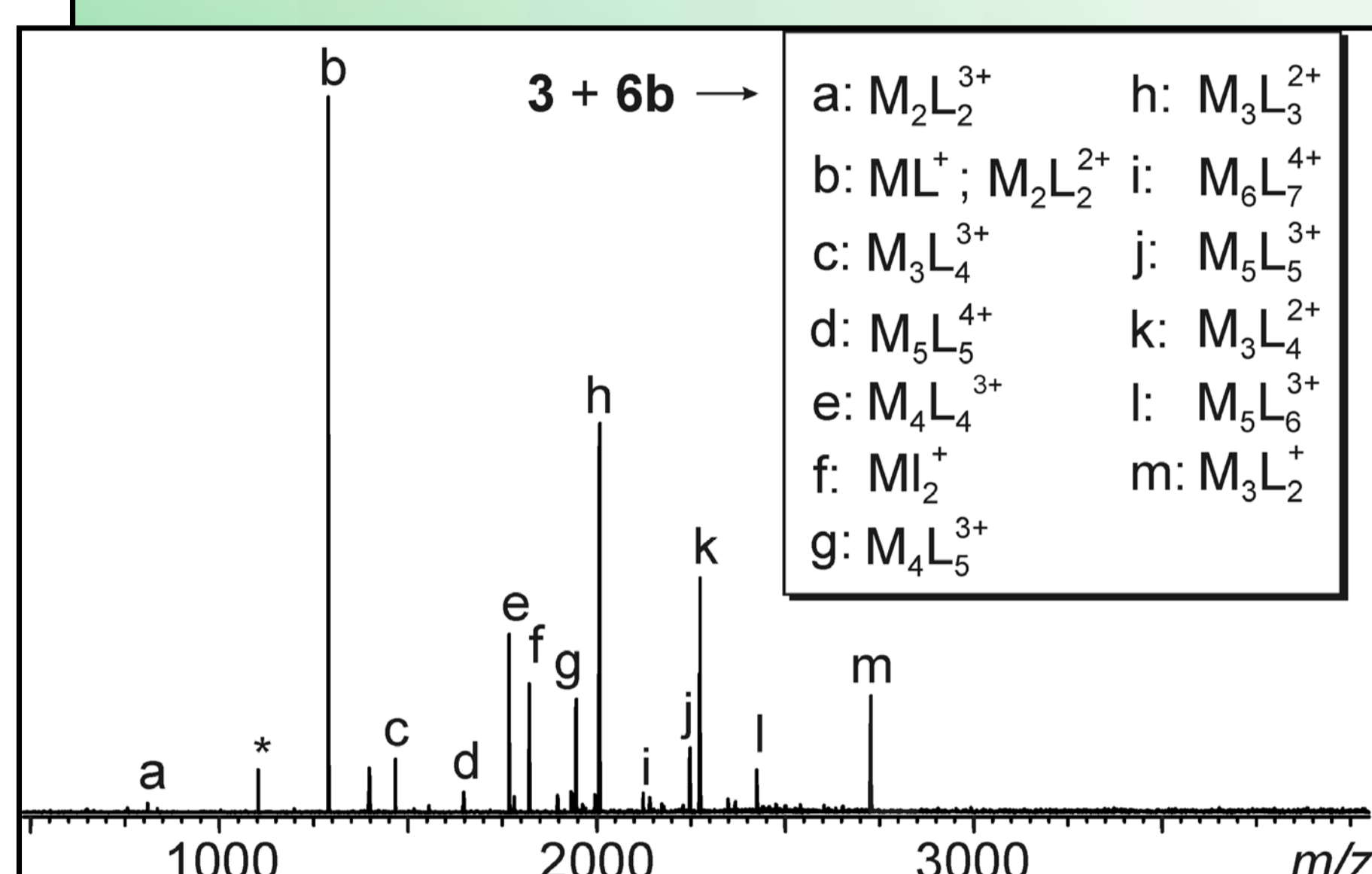
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I. Introduction

Supramolecular coordination polymers are promising candidates for functional molecular devices and nanomaterials. They are formed by metal-directed self-assembly using an organometallic complex or a metal ion and an organic ligand. Here we present a self-assembled coordination polymer formed from a 1:1 mixture of (dppp)M(OTf)₂ (M = Pd(II) and Pt(II)) and a pyridine containing bidentate ligand in organic solvents. Both the limited synthetic effort required in the preparation and the structure control through the synthesis of the building blocks make these polymers good candidates for nanotechnological applications. Moreover, dissolving the coordination polymer in methanol or methanol/water mixtures at room temperature results in vesicle formation which may be used, in general, as drug and gene carriers, nanoreactors, etc.

III. ESI-FTICR mass spectrum of a 1:1 Mixture of 3 and 6b



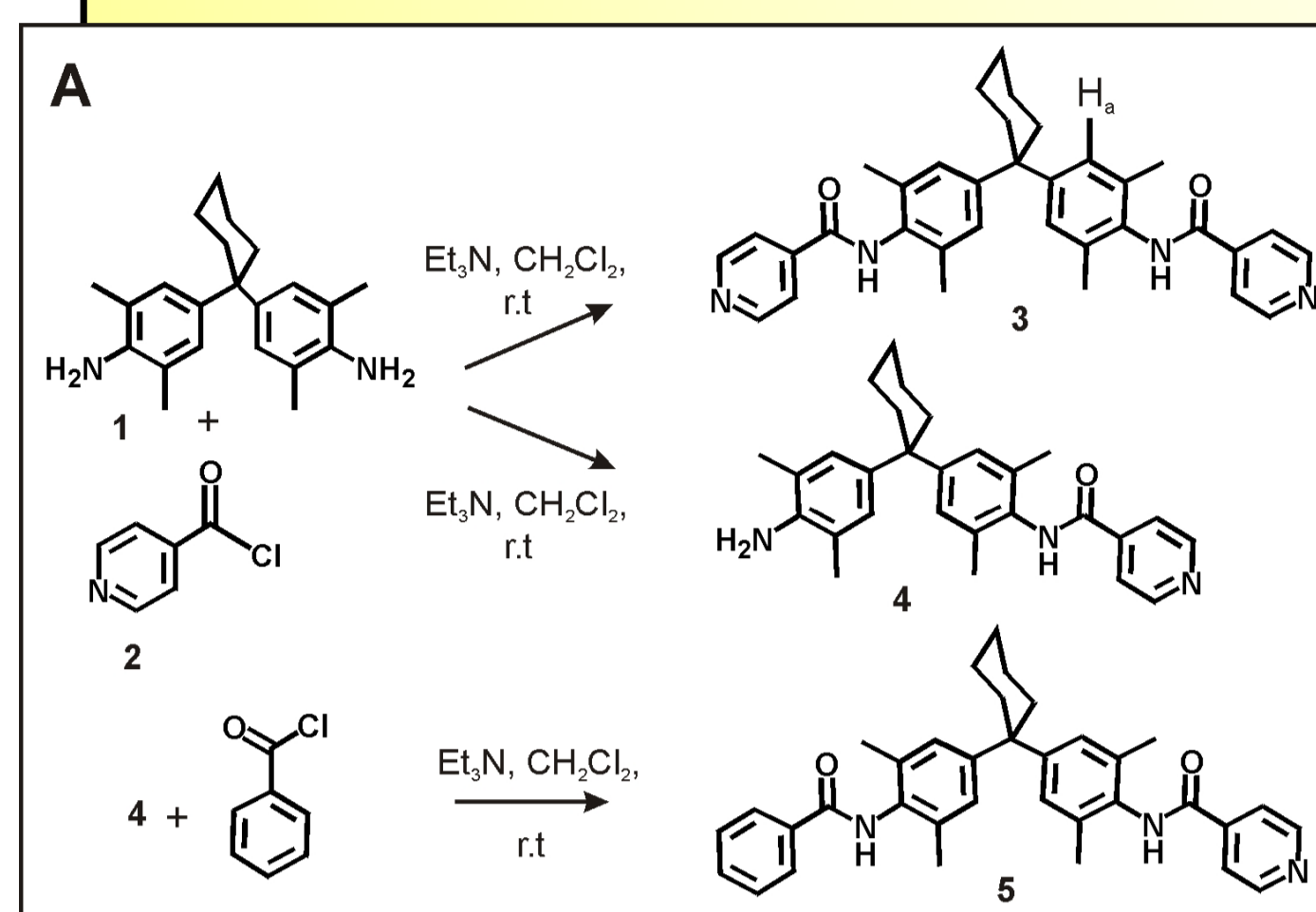
Electrospray-ionization Fourier-transform ion-cyclotron-resonance (ESI-FTICR) mass spectrometry [1]. A 150 μM solution of 7b is sprayed from acetone.

[1] H. T. Baytekin, M. Sahre, A. Rang, M. Engeser, A. Schulz, C. A. Schalley, *Small* **2008**, in press. [iii] F. Würthner, C.-C. You, C. R. Saha-Möller, *Chem. Soc. Rev.* **2004**, 33, 133-146. [iii] C. A. Schalley, T. Müller, P. Linnartz, M. Witt, M. Schäfer, A. Lützen, *Chem. Eur. J.* **2002**, 8, 3538-3551.

Three main conclusions are:

- (1) Oligomers are observed up to the M₆L₇⁴⁺ complex. Assembly formation is thus not restricted to small cycles.
- (2) All signals except signal "m" in Figure 1 (likely a fragment) either correspond to complexes with the same number of corners and ligands (M:L = 2:2, 3:3, 4:4, 5:5) or they bear one ligand more than metal corners (M:L = 1:2, 2:3; 3:4, 4:5, 5:6, 6:7). The first series can be assigned to cyclic, the second to linear oligomers terminated at both ends by a ligand - in line with the fact that the second pyridine binds more strongly to the corner than the first. [1]
- (3) Since some fragmentation usually occurs upon ionization, [1] the average oligomer chain length is likely higher in solution than that observed in the mass spectrum.

II. Synthesis of self-assembled supramolecular polymers and preparation of metallo-supramolecular nano-spheres



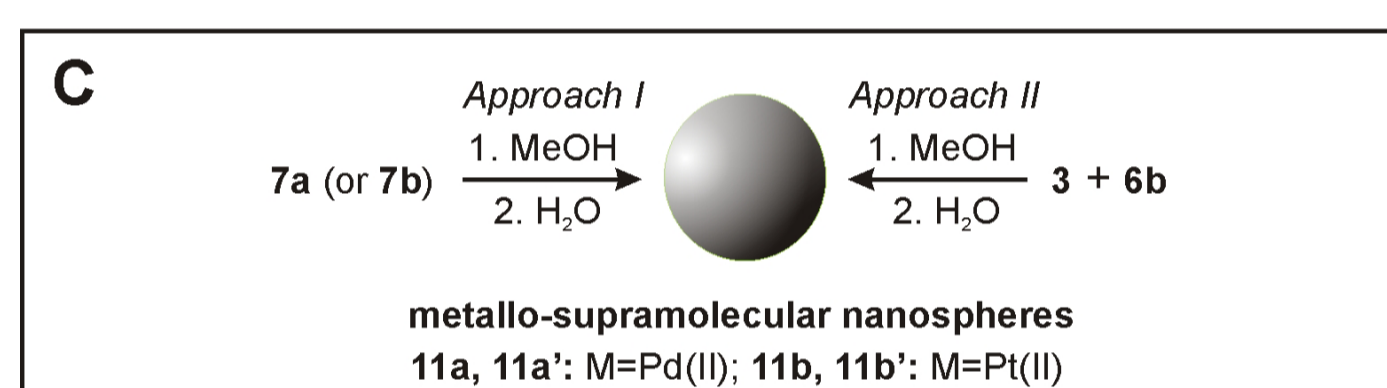
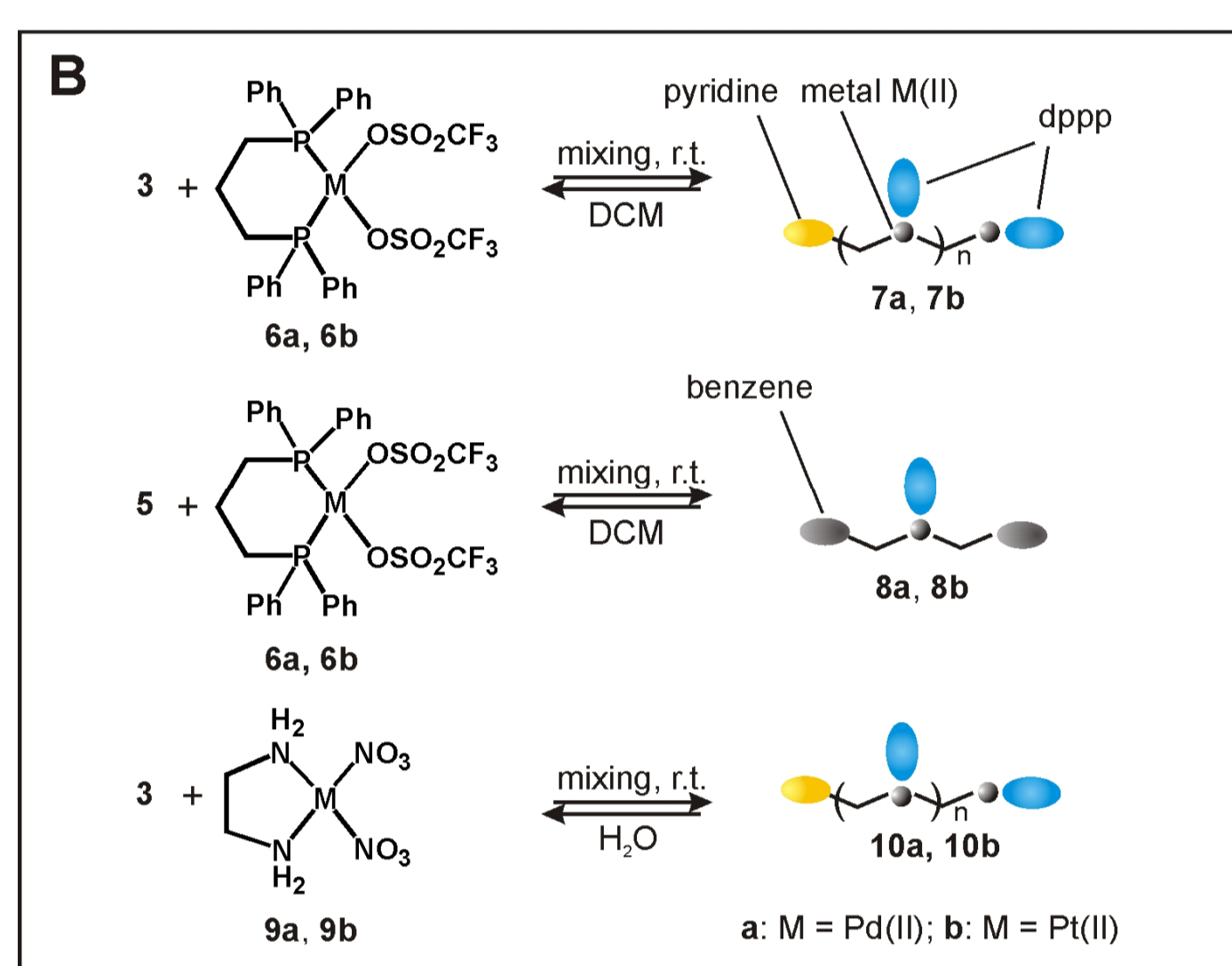
Standard amide-bond formation between Hunter's diamine [1] and isonicotinoyl chloride 2 yields the bent bidentate dipyriddy-substituted ligand 3 [1] which bears two diverging coordination sites (A). For the preparation of coordination polymers, [1] equimolar amounts of the (dppp)M(OTf)₂ precursor complexes (dppp = bis-(diphenylphosphino)propane, OTf = triflate; M = Pd(II) (6a) or M = Pt(II) (6b)) [1] and of ligand 3 were mixed in dichloromethane and stirred for 2 hours. Finally, slow addition of diethyl ether to the reaction mixture resulted in white precipitates of 7a or 7b, respectively, with yields of 95% and 90% (B). When pre-assembled coordination polymers 7a or 7b are dissolved in methanol and heated to 50°C followed by cooling to r.t. and dropwise addition of deionized water, a cloudy suspension is obtained (C).

[ii] a) C. A. Hunter, *J. Am. Chem. Soc.* **1992**, 114, 5303-5311. b) C. A. Hunter, P. S. Jones, P. Tiger, S. Tomas, *Chem. Eur. J.* **2002**, 8, 5435-5446.

[iii] C. A. Hunter, C. M. R. Low, C. Rotger, J. G. Vinter, C. Zonta, *Proc. Natl. Acad. Sci. USA* **2002**, 99, 4873-4876.

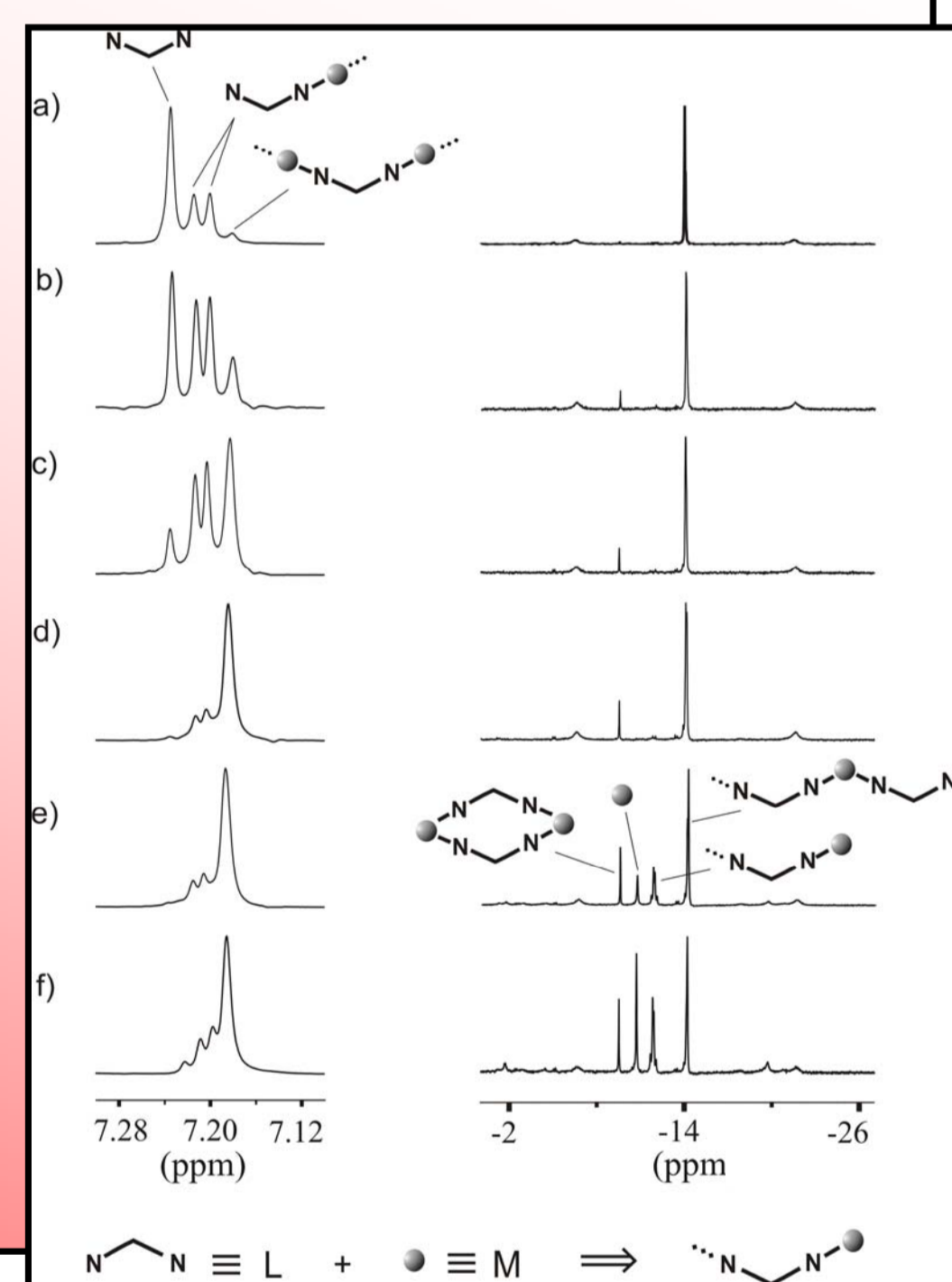
[iii] a) E. C. Constable, W. Meier, C. Nardin, S. Mundwiler, *Chem. Commun.* **1999**, 1483-1484. b) Z. Qin, M. C. Jennings, R. Puddephatt, *Chem. Commun.* **2002**, 354-355. c) T. J. Burchell, D. J. Eisler, R. J. Puddephatt, *Chem. Commun.* **2004**, 944-945. d) H.-J. Kim, W.-C. Zin, M. Lee, *J. Am. Chem. Soc.* **2004**, 126, 7009-7014. e) J. Wm. Wackery, J. S. Moore, *Macromolecules* **2006**, 39, 7269-7276.

[iv] a) P. J. Stang, D. H. Cao, *J. Am. Chem. Soc.* **1994**, 116, 4981-4982. b) P. J. Stang, J. A. Whiteford, *Organometallics* **1994**, 13, 3776-3777.



IV. ¹H and ³¹P-NMR Spectroscopy

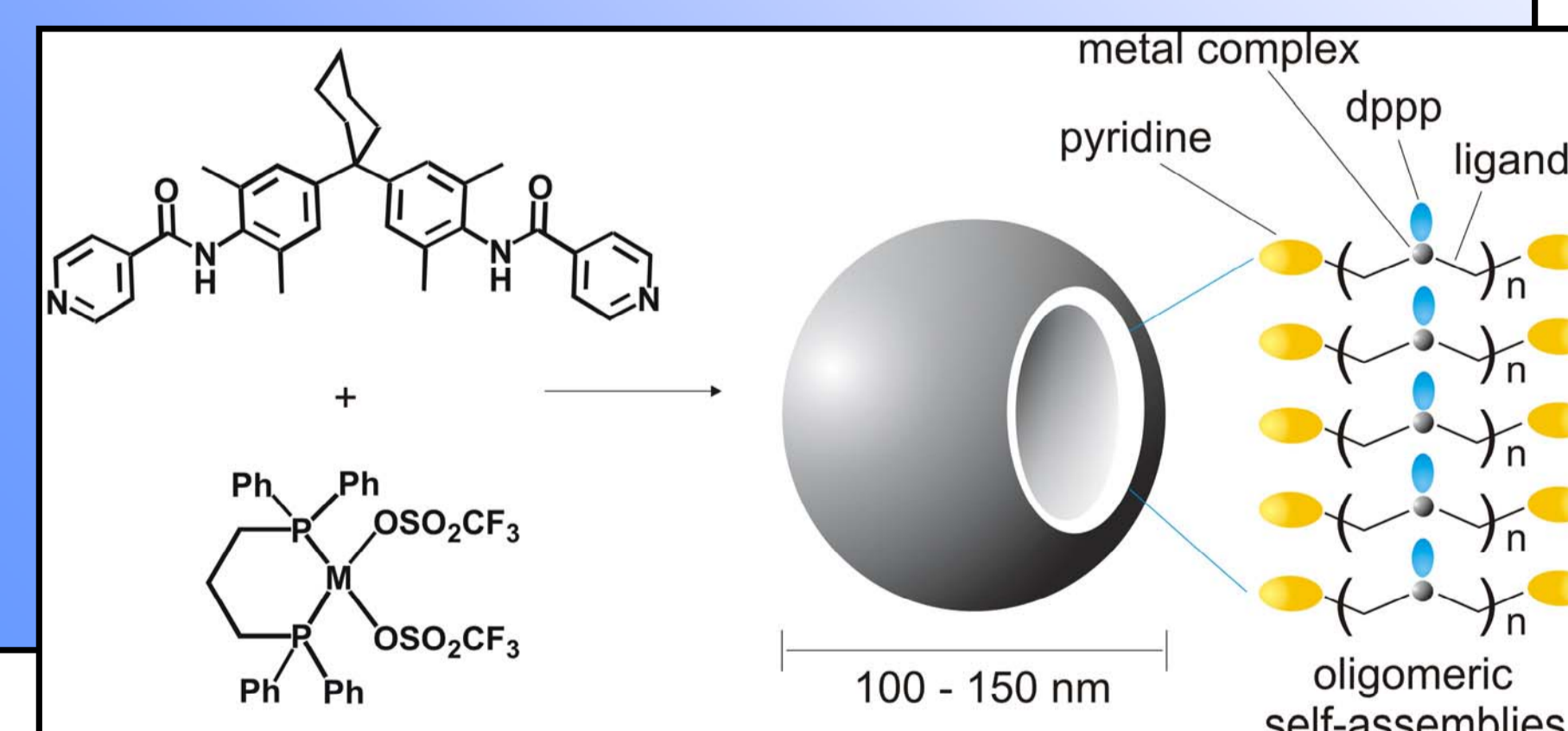
Assembly formation can be monitored by following the signal for the aromatic dimethyl aniline C-H proton Ha and that of the P atoms of the corner. At low corner concentrations (a), free ligand (¹H-NMR signal) is observed next to two signals for singly coordinated and thus unsymmetric ligand (2 signals, 1:1 ratio). All corners are doubly coordinated rendering the P atoms equivalent; only one signal is observed in the ³¹P NMR spectrum. Pyridine coordination is confirmed by a ¹J_{P-Pt} coupling constant of 3041 Hz ((dppp)Pt(OTf)₂ precursor: 3647 Hz). Upon increasing corner concentration, an additional ¹H-NMR signal appears which grows to become the major one at a corner : ligand ratio of 1:1 (d). It is a signal for doubly coordinated ligand as appearing in cyclic or along the middle of the chains in linear oligomers. For a corner:ligand ratio of 1:1, all corners are still doubly substituted in line with the mass spectra and binding energies. A small, somewhat strained cyclic 2:2 assembly may be responsible for the additional small peak appearing downfield from the major one in the ³¹P-NMR spectrum. If the corner concentration is higher than that of the ligand, singly substituted corners appear as double doublets (the two P atoms at these corners are non equivalent and couple with each other). A singlet for the free corner becomes also visible. In line with earlier data, ligand exchange is fast on the NMR time scale at r.t. for 7a. Only one averaged set of signals is observed.



VI. Structural Model

Based on these analytical results, we suggest the structural model shown below. Coordination oligomers cross the vesicle wall and can be connected among each other by;

- electrostatic interactions between the cationic metal centers and intermittent counterions,
- hydrogen bonds between the amide groups,
- Van-der-Waals and hydrophobic interactions between the backbones. On both ends, the coordination oligomers have basic pyridines which are at least partially protonated and form hydrogen bonds to the surrounding water thus leading to the formation of a wall which is solvated on both sides by water - inside the vesicle and outside.



V. Transmission Electron Microscopy

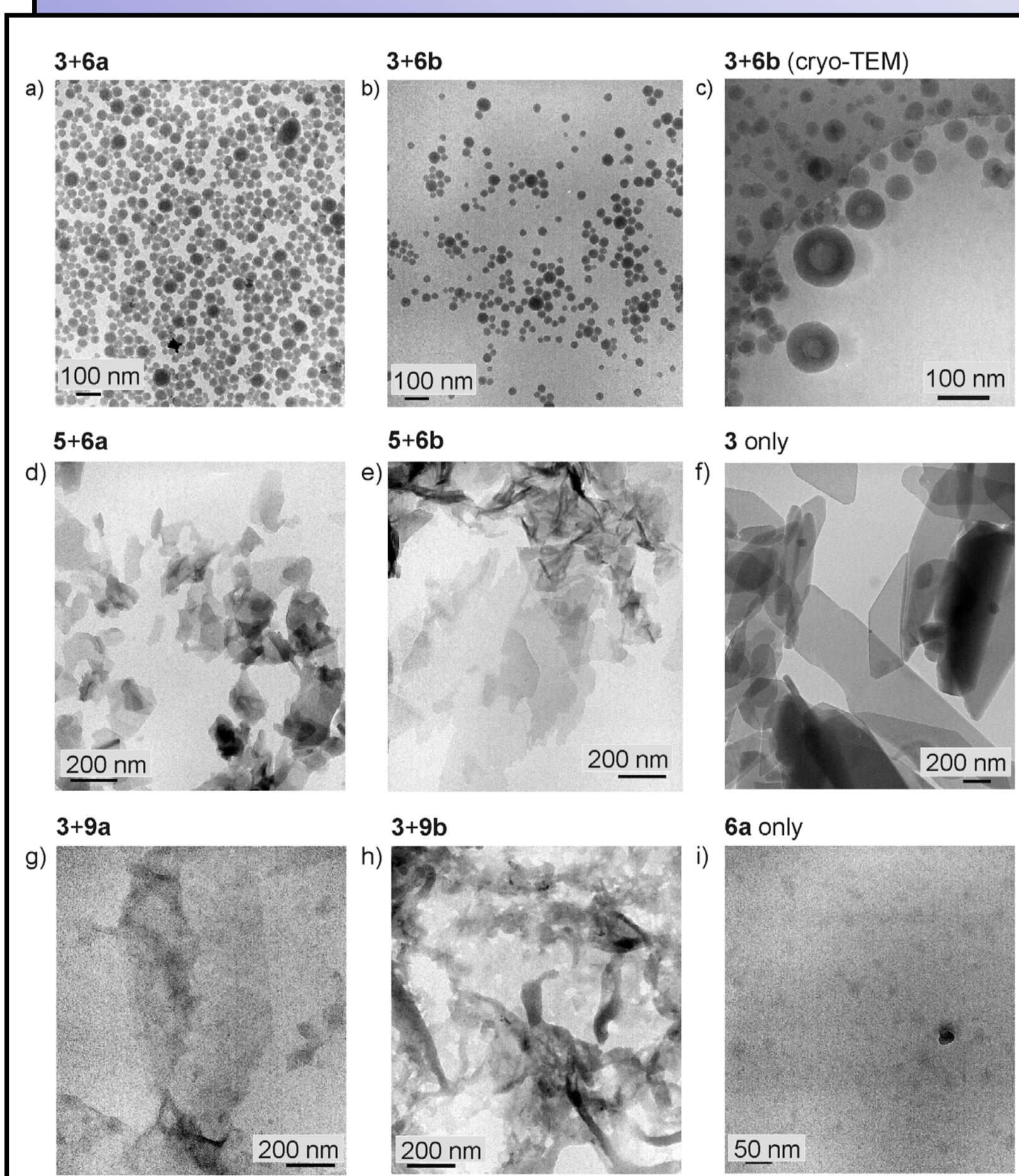
Evidence for the formation of vesicles from these metallo-supramolecular oligomers comes from (cryogenic) transmission electron microscopy (TEM, cryo-TEM). Pd(II) and Pt(II) metal complexes formed nano-spheres with ligand 3, see (a-c).

Representative TEM images of

- 9a' (2 mg/mL) in 40 % MeOH/H₂O after sonication for 15 min;
 - 9b' (1 mg/mL) in 40 % MeOH/H₂O after sonication for 15 min; and
 - cryo-TEM image of 9b' (1 mg/mL) in 40 % MeOH/H₂O after sonication for 15 min.
- All of these metallo-spheres were prepared using approach II.

Moreover, the following control experiments showed that:

- Ligand 3 alone leads to monolayer formation.
- Pt(II) corner 6b gave much smaller black dots in the TEM images - probably nano-crystals.
- Metal complexes 8a,b formed from monodentate ligand 5 result in crystalline mono-layered structures.
- The use of ligand 3 together with water soluble Fujita-type (en)M(II)(NO₃)₂ metal complexes, (9a: M = Pd; 9b: M = Pt) as the corners did not lead to the formation of round-shaped objects. Consequently, the nano-spheres require a bidentate ligand such as 3 and the use of Stang-type corners 6a,b. Both building blocks are obviously required and the formation of coordination oligo- or polymers is likely a prerequisite for vesicle formation, because no vesicles are observed with the much shorter 2:1 complexes 8a,b. The ancillary ligand (dppp vs. en) on the metal center also plays an important role by adjusting solubilities just right for aggregation to occur.



VII. Conclusions

Metal-directed self-assembled vesicles were prepared using a little synthetic effort. Mixing two of the building blocks of a vesicle (compounds 3) and (6a,b) at room temperature in methanol or in aqueous methanol solution with and without an ultrasonic shaker at r.t. resulted in nanometer sized vesicles. Ultrasonic shaking resulted in a more homogenous size distribution. Pd(II) assemblies result in broadened signals in a ¹H-NMR spectrum in DMF at r.t. However, Pt(II) assemblies exhibited a rather complex ¹H and ³¹P-NMR spectra.

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