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Self-Assembly of a Nanoscopic $Pt_{12}Fe_{12}$ Heterometallic Open Molecular Box Containing Six Porphyrin Walls**

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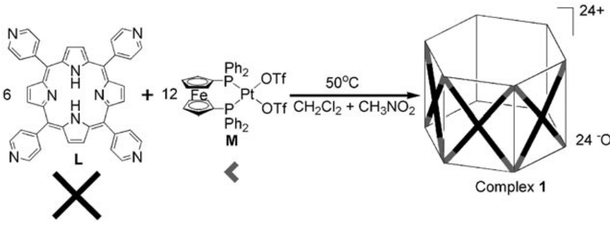
Coordination-driven self-assembly has proven to be an efficient approach towards the synthesis of large supramolecules of finite shapes and sizes, as reflected in the literature.[1–2] Square-planar Pd^{II} and Pt^{II} centers have long been among the favorite choices for this purpose because of their rigid coordination environments. Several 3D closed architectures such as spheres, dodecahedrons, prisms, and trigonal bipyramids, have been prepared by using these metal ions in conjunction with suitable polypyridyl linkers.[3] The properties of a molecule depend on the functional group(s) present. Thus, incorporation of functional groups into nanostructures may be an efficient way to guide the properties of the resulting assemblies. Porphyrin derivatives are important in biological systems for oxygen transport, energy conversion, and electron transfer. Thus, the construction of porphyrin-based discrete assemblies is a promising approach in the field of designed self-assembly. Surprisingly, the introduction of porphyrin functionality into discrete nanoscopic architectures of Pd^{II}/Pt^{II} centers is much less developed.[4] Moreover, among the several 3D discrete assemblies reported, a molecular box is one of the much less known architectures.[4a–b,5] The use of a tetratopic unit is the right choice for designing such a system. However, all the preceding examples of molecular boxes contain either three or four faces occupied by the tetratopic unit, whereas an example of a large discrete open box containing six such faces is not yet known. Herein we report the design and synthesis (Scheme 1) of the first $Pt_{12}Fe_{12}$ heterometallic open hexagonal box (**1**) containing six faces occupied by six 5,10,15,20-tetrakis(4-pyridyl)porphyrin (L) linkers.

The molecular box $[\{cis\text{-(dppf)Pt}\}_{12}(L)_6](OTf)_{24}$ (**1**; dppf = 1,1′-bis(diphenylphosphino)ferrocene; OTf = $CF_3SO_3^-$) was obtained in 94 % yield by reaction of a solution of the pseudo-C_4-symmetric tetratopic donor L in dichloromethane with two equivalents of *cis*-$[(dppf)Pt(OTf)_2]$ (M) in nitromethane for 2 h (Scheme 1). An immediate sharp change in color of the solution of L from violet blue to red brown upon addition of *cis*-$[(dppf)Pt(OTf)_2]$ was an indication of the reaction. The final product was isolated as a red-brown solid by adding diethyl ether.



Scheme 1. Synthesis of the hexagonal open box **1**.

The self-assembly of the tetratopic donor linker L with two equivalents of suitable 90° Pt^{II} acceptor M may lead to the formation of several discrete open or closed architectures (Scheme 2) in which the tetratopic ligands span the faces and 90° Pt^{II} acceptors occupy the vertices.

It is well established that the same set of donor and acceptor may sometime produce a mixture of structural isomers, which show distinctly different peaks in phosphorus NMR spectroscopy.[5c] In the present case, the $^{31}P\{^1H\}$ spectrum of the assembly showed a sharp single peak at $\delta = 4.09$ ppm in $CDCl_3$ with concomitant ^{195}Pt satellites (see the Supporting Information). An upfield shift of about 5 ppm of the phosphorus peak in the product from the starting complex *cis*-$[(dppf)Pt(OTf)_2]$ was a clear indication of the ligand-to-metal coordination and the formation of a single product.

The ^1H NMR spectrum of **1** was also indicative of the symmetrical arrangement of the linkers and displayed significant differences from the spectra of the precursor building blocks (Figure 1 and Supporting Information). Significant downfield shift ($\Delta\delta = 0.7$ ppm) of the α-pyridyl protons as well as the appearance of NH protons in the final product were in support of the coordination of the pyridyl nitrogen atoms to the *cis*-$\{Pt(dppf)\}^{2+}$ unit and the presence of an unoccupied porphyrin N_4 pocket. However, the room temperature ^1H and ^{31}P NMR spectra cannot conclude the actual composition of the product; rather, it can only confirm the ligand to metal coordination and the formation of a single product.

Finally, ESI mass spectrometry clearly confirmed a $M_{12}L_6$ stoichiometry from a series of prominent peaks of $[\mathbf{1}-(OTf)_n]^{n+}$. The peaks at *m*/*z* 1478.2, 1207.7, 1013.2, 867.7,

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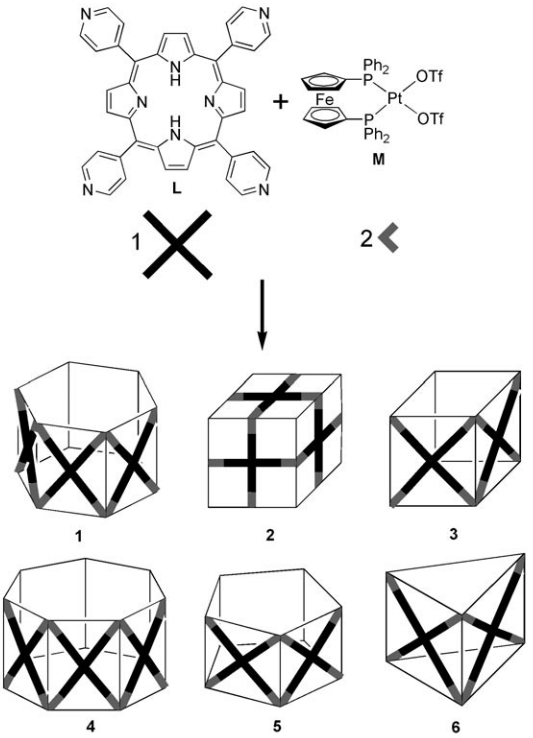

Scheme 2. A few possible discrete architectures from the 1:2 self-assembly of L and M.

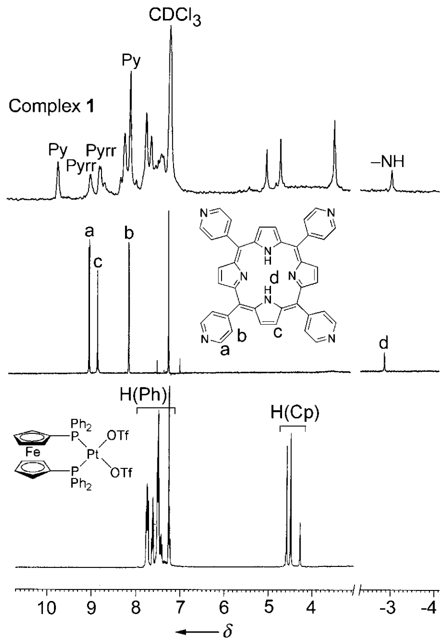

Figure 1. ^1H NMR spectra of the complex **1** and linkers L and M in $CDCl_3$.

and 754.2 were assigned to $[\mathbf{1}-(OTf)_{10}]^{10+}$, $[\mathbf{1}-(OTf)_{12}]^{12+}$, $[\mathbf{1}-(OTf)_{14}]^{14+}$, $[\mathbf{1}-(OTf)_{16}]^{16+}$, and $[\mathbf{1}-(OTf)_{18}]^{18+}$, respectively (Supporting Information).

Two structural isomers are possible for a [12+6] self-assembled complex of the *cis*-protected ditopic acceptor M and the tetratopic donor L corresponding to different orientations of the building units: a hexagonal open box **1** containing six porphyrin walls and a closed cube **2** with the same number of walls (Scheme 2).

These two isomers cannot be distinguished by mass spectroscopy. However, in principle, NMR spectroscopy can distinguish these two isomers. The presence of a single peak in the ^{31}P NMR established the formation of any one of these two isomeric architectures (**1** or **2**). All the CH pyrrolyl protons in the cubic analogue must be identical, whereas in the case of the hexagonal open barrel two different sets of CH pyrrolyl protons are expected. The room temperature NMR spectrum showed only two sets of signals ($\delta = 9.80$ and 8.10 ppm) for α and β protons of the pyridyl moieties and two peaks ($\delta = 9.06$ and 8.85 ppm) arising from the pyrrolyl protons. The pyrrolyl protons in the free ligand L appeared as a singlet at $\delta = 8.86$ ppm. The pyridyl protons showed only two peaks (α and β) even at low temperature (Supporting Information) because of the low energy barrier of Pt−N(pyridyl) bond rotation as well as the free rotation of the C(pyridyl)−C(porphyrin) bond. The assignments of the pyridyl and pyrrolyl protons are based on the relative integration of the peaks and comparison with the reported porphyrin assemblies.[4a,e] Finally, the H–H COSY NMR spectrum of **1** in $CDCl_3$ showed clear correlation between the α- and β-pyridyl protons, which also confirms our assignment (see the Supporting Information). To avoid steric interaction among the bulky dppf moieties, the wider barrel **1** is expected to be energetically more favorable than the more compact closed analogue **2**.

In fact, the formation of the structural isomer **1** was confirmed by X-ray analysis.[6] Single crystals of **1** were obtained by slow vapor diffusion of diethyl ether into a solution of **1** in CH_3NO_2/CH_2Cl_2. X-ray diffraction studies showed the formation of an unusual hexameric open box (Figure 2). The crystal structure of **1** clearly demonstrates that the six porphyrin-based units are hinged by twelve *cis*-$\{(dppf)Pt\}^{2+}$ building blocks to form Pt_6 hexameric rings on the top and bottom of the box. The box structure of **1** is very rigid, and the inner cavity is extraordinarily large. The framework has a dimension of $27 \times 27 \times 19$ Å^3, and the internal void volume is estimated to be approximately 43 550 Å^3, which is very large for a discrete open coordination cage.

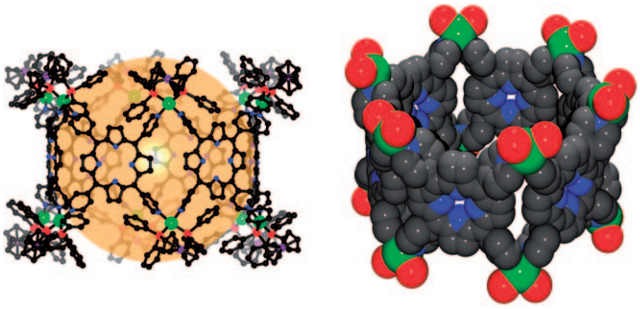

Figure 2. Ball and stick (left) and CPK (right) view of the molecular structure of **1** (green Pt, violet Fe, red P, blue N, black C). Ferrocenyl moieties and phenyl rings are omitted in the CPK view.

The Py−Pt−Py bite angles (80.03–80.53°) were slightly less than the ideal angle (90°) for square-planar environment. In contrast, the P−Pt−P bite angles were (99.80–100.08°) slightly larger than the ideal value. The shortest Pt⋯Pt distance within the cluster was measured to be 13.18 Å and the distance between the opposite Pt centers of the hexagonal ring was 27.2 Å, which measured the diameter of the box. The packing diagram showed the formation of nanoscopic hexagonal pores in the solid state (Figure 3). The shortest intermolecular Pt⋯Pt distance is 11.2 Å. The distance between the centroids of the N_4 macrocycles of the two opposite porphyrin moieties in the box is 23.2 Å, which indicates that the middle of the box is slightly squeezed (from an ideal value of 23.4 Å for a perfect hexagon). Two phenyl rings of the dppf are oriented away from the Pt_6 ring, and the other two phenyl rings are tilted towards the ring with weak π–π interaction between the phenyl and pyridyl rings. The centroids of two cyclopentadienyl (Cp) rings of each dppf moiety are not exactly parallel to the two phosphorus donors; rather one Cp ring is slightly tilted toward the Pt_6 ring.

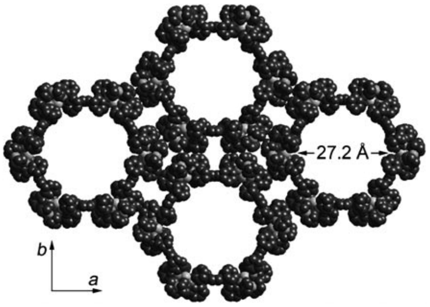

Figure 3. Packing view of complex **1** down the crystallographic *c* axis showing the formation of hexagonal channels of diameter 27.2 Å.

In a variable-temperature ^{31}P NMR experiment, the splitting of the ^{31}P peak at low temperature (Figure 4) can be explained by the crystal structure. In the solid state, two phosphorus nuclei attached to a Pt center are not in perfectly magnetically identical environments. One Cp ring along with the PPh_2 group of dppf moiety is tilted toward the interior of the molecule while the other is tilted toward the exterior. A singlet peak in the ^{31}P NMR spectrum recorded at room temperature can be attributed to the rapid twisting of the ferrocenyl moiety with respect to the Pt metal center and thereby seeming identical phosphorus nuclei to NMR time scale. Upon lowering the temperature, the peak splits into a doublet (Figure 4) because of the conformationally frozen ferrocenyl moieties.

The development of optical sensors for trace metals is of great interest to chemists and will have applications in environmental and biomedical fields.[7] Zinc is the next most abundant 3d transition metal after iron in the human body. Moreover, it has several important functions in biological processes. Fluorescence spectroscopic techniques can be a useful tool for zinc assays. Porphyrin derivatives are characteristic chromophores because of their: 1) high absorption coefficient at 400–500 nm; 2) tunable fluorescence emission with a concomitant modification of molecular structure; 3) large Stokes' shift, which reduces the effects of background fluorescence.[8] Hexagonal box **1** has six porphyrin pockets for binding metal ions of appropriate size and is soluble in common polar solvents such as nitromethane, methanol, and dichloromethane. It has high encapsulating efficiency toward Zn^{2+} at room temperature without any catalyst.[9] Titration of this box with the required amount of zinc(II) acetate showed a dramatic change in color from red brown to dark green, while the basic structure of the box remained intact. Absorption, fluorescence, and NMR spectroscopic studies indicated the encapsulation of Zn^{II} ions into the N_4 pocket of the porphyrin rings occupying the walls of the box.

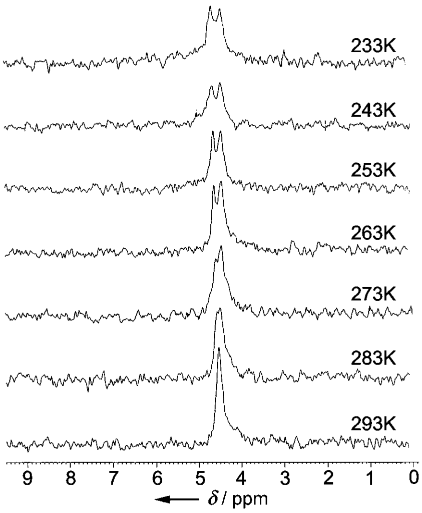

Figure 4. Variable-temperature ^{31}P NMR spectra of the complex **1** in CD_3OD.

The electronic spectrum of **1** (shown as dotted line in Figure S6 in the Supporting Information) exhibited an intense Soret band at 414 nm along with a series of four Q bands present at 510, 544, 587, and 643 nm originating from the porphyrin moiety. All these bands are red shifted with respect to complex **1** upon addition of Zn^{II}. The spectra are marked by broadening and an increase in the intensity of the Soret band upon titration with increasing amounts of Zn^{II}. The Q bands, however, in addition to being red shifted, decrease in intensity for the bands at 510, 587, and 643 nm, while the band at 544 nm is shifted considerably to 556 nm accompanied by increase in intensity with increasing amount of Zn^{II}. The spectral change observed is indicative of the coordination of Zn^{II} ion into the porphyrin pocket with concomitant deprotonation of the porphyrin NH groups. The fluorescence spectrum of **1** (Figure 5) displays two emission peaks at 646 and 709 nm very similar in shape and position to that of L. The fluorescence emission is characterized by the enhancement of the emission bands at 646 and 709 nm upon addition of a 1/6 equivalent of Zn^{II} to a methanolic solution of **1** along with the development of new band at 609 nm. Figure 5 shows the spectral change following the addition of increasing amount of Zn^{II} to **1**. While the band at 709 nm is quenched with addition of increasing amount of Zn^{II}, the band at 646 nm remains essentially unchanged. Such spectral changes are due to the binding of the Zn^{II} in the porphyrin N_4 pocket.

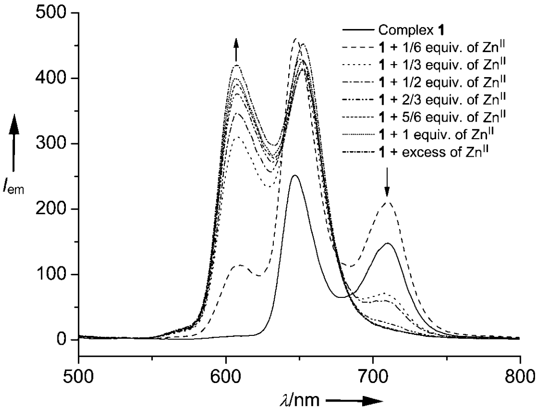

Figure 5. Emission fluorescence spectra of a methanolic solution of **1** (2×10^{-6} м) upon addition of increasing amounts of Zn^{II}.

In conclusion, six porphyrin-based tetratopic building blocks intermolecularly bind twelve 90° Pt^{II}-based acceptors in a self-assembled manner, resulting in the formation of the first hexagonal open molecular box of Pt^{II}. Although a few extended complexes of transition metals with a 5,10,15,20-tetrakis(4-pyridyl)porphyrin linker are known,[10] no discrete metal assembly containing this linker has been reported so far. Although the formation of a large ensemble from many starting components is entropically less favorable than for the smaller analogue using same set of donor and acceptor, the use of a bulky dppf blocked linker helped us to obtain the wider hexagonal box rather than the more compact smaller analogues (Scheme 2). Thus, the present results demonstrate that large porphyrin-functionalized supramolecules can be constructed in a single step by using appropriate linkers. Preliminary investigation showed the enhancement of the solution fluorescence of the box upon binding Zn^{II}. Porphyrin-mediated molecular recognition, host–guest chemistry, and the possibility of using this and some related assemblies as a fluorescent sensor are currently under investigation, and the results will be reported elsewhere.

Experimental Section

A solution of *cis*-[(dppf)Pt(OTf)$_2$] (21.0 mg, 0.02 mmol) in nitromethane (4 mL) was added drop by drop to a solution of 5,10,15,20-tetrakis(4-pyridyl)porphyrin (6.2 mg, 0.01 mmol) in dichloromethane (2 mL) in a 10 mL round-bottom flask with continuous stirring for 15 min. A distinct color change from violet blue to red brown was observed. The mixture was further stirred for 2 h at 50°C. After cooling the reaction mixture to room temperature, diethyl ether was added to isolate the product as brown precipitate (**1**). Yield: 25.4 mg (94%). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.4 MHz): $\delta = 4.09$ ppm (s); (CD$_3$OD, 121.4 MHz): $\delta = 4.51$ ppm (s). ^{1}H NMR: $\delta = 9.8$ (8H, Py); 9.06 (4H, Pyrr); 8.85 (4H, Pyrr); 8.10 (8H, Py); 8.30 (8H, Ph); 7.73–7.32 (32H, Ph); 5.0–3.46 (16H, Cp); −3.16 ppm (2H, NH). Anal. calcd for $C_{672}H_{492}F_{72}Fe_{12}N_{48}O_{72}P_{24}Pt_{12}S_{24}$: C 49.57, N 4.13, H 3.05%; found: C 49.83, N 4.40, H 3.28%. The Zn^{II}-coordinated derivative of **1** was obtained by treating a solution of **1** with a methanolic solution of 6 equivalents of Zn^{II} acetate.

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[1] a) S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem.* **2002**, *114*, 938–993; *Angew. Chem. Int. Ed.* **2002**, *41*, 898–952; b) C. A. Schalley, K. Beizai, F. Vögtle, *Acc. Chem. Res.* **2001**, *34*, 465–476; c) J.-M. Lehn, *Chem. Eur. J.* **1999**, *5*, 2455–2463; d) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983; e) P. H. Dinolfo, J. T. Hupp, *Chem. Mater.* **2001**, *13*, 3113–3125; f) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908; g) C. A. Schalley, T. Müller, P. Linnartz, M. Witt, M. Schäfer, A. Lützen, *Chem. Eur. J.* **2002**, *8*, 3538–3551; h) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975–982; i) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509–518; j) R. W. Saalfrank, A. Scheurer, R. Puchta, F. Hampel, H. Maid, F. W. Heinemann, *Angew. Chem.* **2007**, *119*, 269–272; *Angew. Chem. Int. Ed.* **2007**, *46*, 265–268; k) N. L. Toh, M. Nagarathinum, J. J. Vittal, *Angew. Chem.* **2005**, *117*, 2277–2281; *Angew. Chem. Int. Ed.* **2005**, *44*, 2237–2241.

[2] a) H.-B. Yang, K. Ghosh, Y. Zhao, B. H. Northrop, M. M. Lyndon, D. C. Muddiman, H. S. White, P. J. Stang, *J. Am. Chem. Soc.* **2008**, *130*, 839–841; b) H.-B. Yang, K. Ghosh, B. H. Northrop, Y.-R. Zheng, M. M. Lyndon, D. C. Muddiman, P. J. Stang, *J. Am. Chem. Soc.* **2007**, *129*, 14187–14189; c) P. S. Mukherjee, N. Das, Y. K. Kryschenko, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2004**, *126*, 2464–2473; d) J. Chai, V. Jancik, S. Singh, H. Zhu, C. He, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, N. S. Hosmane, *J. Am. Chem. Soc.* **2005**, *127*, 7521–7528; e) S. Ghosh, P. S. Mukherjee, *Organometallics* **2007**, *26*, 3362–3367; f) K. Suzuki, M. Kawano, S. Sato, M. Fujita, *J. Am. Chem. Soc.* **2007**, *129*, 10652–10653; g) M. Tominaga, K. Suzuki, T. Murase, M. Fujita, *J. Am. Chem. Soc.* **2005**, *127*, 11950–11951; h) P. H. Dinolfo, V. Coropceanu, J.-L. Brédas, J. T. Hupp, *J. Am. Chem. Soc.* **2006**, *128*, 12592–12593.

[3] a) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter, P. J. Stang, *Nature* **1999**, *398*, 796–799; b) S. Leininger, J. Fan, M. Schmitz, P. J. Stang, *Proc. Nat. Acad. Sci. USA* **2000**, *97*, 1380–1384; c) S. Ghosh, P. S. Mukherjee, *J. Org. Chem.* **2006**, *71*, 8412–8416; d) P. S. Mukherjee, N. Das, P. J. Stang, *J. Org. Chem.* **2004**, *69*, 3526–3529; e) S. Ghosh, P. S. Mukherjee, *Organometallics* **2008**, *27*, 316–319; f) R. W. Saalfrank, I. Bernt, E. Uller, F. Hampel, *Angew. Chem.* **1997**, *109*, 2596–2599; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2482–2485; g) R. W. Saalfrank, C. Deutscher, S. Sperner, T. Nakajima, A. M. Ako, E. Uller, F. Hampel, *Inorg. Chem.* **2004**, *43*, 4372–4382; h) J. Hu, R. Lin, J. H. K. Yip, K.-Y. Wong, D.-L. Ma, J. J. Vittal, *Organometallics* **2007**, *26*, 6533–6543.

[4] a) N. Fujita, K. Biradha, M. Fujita, S. Sakamoto, K. Yamaguchi, *Angew. Chem.* **2001**, *113*, 1768–1771; *Angew. Chem. Int. Ed.* **2001**, *40*, 1718–1721; b) A. Ikeda, M. Ayabe, S. Shinkai, S. Sakamoto, K. Yamaguchi, *Org. Lett.* **2000**, *2*, 3707–3710; c) J. Fan, J. A. Whiteford, B. Olenyuk, M. D. Levin, P. J. Stang, E. B. Fleischer, *J. Am. Chem. Soc.* **1999**, *121*, 2741–2752; d) S. J. Lee, K. L. Mulfort, X. Zuo, A. J. Goshe, P. J. Wesson, S. T. Nguyen, J. T. Hupp, D. M. Tiede, *J. Am. Chem. Soc.* **2008**, *130*, 836–838; e) E. Lengo, E. Zangrando, R. Minatel, E. Alessio, *J. Am. Chem. Soc.* **2002**, *124*, 1003–1013.

[5] a) Y. Yamanoi, Y. Sakamoto, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2001**, *123*, 980–981; b) S. C. Johannessen, R. G. Brisbois, J. P. Fischer, P. A. Grieco, A. E. Counterman, D. E. Clemmer, *J. Am. Chem. Soc.* **2001**, *123*, 3818–3819; c) M. Ferrer, M. Mounir, O. Rossell, E. Ruiz, M. A. Maestro, *Inorg. Chem.* **2003**, *42*, 5890–5899.

[6] Crystal data for compound **1**: $C_{2016}H_{1476}F_{216}Fe_{36}N_{144}O_{216}P_{72}Pt_{36}S_{72}$, $M_w = 48819.88$, trigonal, space group $R\bar{3}m$, $a = b = 59.826(2)$ Å,

$c = 82.954$ (3) Å, $T = 150$(K), $V = 257\,627(4)$ Å^3, reflections collected = 89243, unique reflections = 21 033 [$R_{\text{int}} = 0.0756$], $R1 = 0.1176$ and $wR2 = 0.3396$. CCDC 698827 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[7] C.-Y. Li, X.-B. Zhang, Y.-Y. Dong, Q.-J. Ma, Z.-X. Han, Y. Zhao, G.-L. Shen, R.-Q. Yu, *Anal. Chim. Acta* **2008**, *616*, 214 – 221, and references therein.

[8] a) R. Grigg, W. D. J. A. Norbert, *J. Chem. Soc. Chem. Commun.* **1992**, 1298 – 1300; b) S. Abad, M. Kluciar, M. A. Miranda, U. Pischel, *J. Org. Chem.* **2005**, *70*, 10565 – 10568.

[9] a) E. Bellacchio, S. Gurrieri, R. Lauceri, A. Magrì, L. M. Scolaro, R. Purrello, A. Romeo, *Chem. Commun.* **1998**, 1333 – 1334; b) R. Yang, K. Li, K. Wang, F. Zhao, N. Li, F. Liu, *Anal. Chem.* **2003**, *75*, 612 – 621.

[10] T. Ohmura, A. Usuki, K. Fukumori, T. Ohta, M. Ito, K. Tatsumi, *Inorg. Chem.* **2006**, *45*, 7988 – 7990, and references therein.