Mesoscopic Globular Self-assemblies of Platinum(II) Complexes Containing Porphyrins

Mariangela Castriciano,[a] Andrea Romeo,[a] Raffaello Romeo,[a] and Luigi Monsu′ Scolaro*[a,b]

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Slow evaporation of an acetone or chloroform solution of the novel tetranuclear platinum(II) complex [Pt(Lau$_2$dim)Me]$_4$(TpyP)(CF$_3$SO$_3$)$_4$ [Lau$_2$dim = didodecyldiimine; TpyP = 5,10,15,20-tetrakis(4-pyridyl)-21*H*,23*H*-porphyrin] on a glass surface affords globular micrometric sized aggregates.

Introduction

The formation of organized supramolecular structures of chromophores with well-defined shapes and sizes is a topic of relevant interest.[1] Their potential application in energy storage and conversion, supramolecular catalysis, optics and electronics can be easily recognized. In this respect, porphyrins and their metal derivatives are important compounds due to their favorable photophysical, electronic and catalytic properties. These features are strictly related to their aggregation state and strongly depend on the microstructural environment.[2] Specifically tailored porphyrins can be easily dissolved in micelles or liposomes[3] obtaining systems that assume the required stability, rigidity and orientation to perform specific functions, for example to mimic cytochrome P-450.[4] Amphiphilic porphyrins have been exploited in the preparation of simple micelles,[5] fibers[6] and vesicles,[7] while "octopus" porphyrins have shown their tendency to self-assemble in vesicles[8] or fibers[9] able to bind oxygen in an aqueous medium. The formation of porphyrin wheels or rings in the mesoscopic range has been achieved by simple solvent evaporation.[10]

Metal complexes can be conveniently exploited to synthesize properly modified porphyrins[11] or linked porphyrin arrays using the self-assembly idea.[12] We have recently reported on the application of platinum(II) organometallic complexes to the synthesis of tetrasubstituted porphyrins that are soluble in micellar phases.[13] We knew from a detailed kinetic investigation on cationic complexes of the type [Pt(N-N)Me(Me$_2$SO)]$^+$ (N-N = a series of diamines or diimines)[14] that the coordinated Me$_2$SO becomes very labile when N-N is a diimine. Therefore, we used the complex [Pt(Cy$_2$dim)Me(Me$_2$SO)]$^+$ (Cy$_2$dim = dicyclohexyldiimine) as a monofunctional building block for introducing the platinum molecular fragment and for accessing a specifically tailored porphyrin.[13]

This paper describes the formation of globular mesoscopic aggregates by simple evaporation of solutions containing a novel 5,10,15,20-tetrakis(4-pyridyl)-21*H*,23*H*-porphyrin (TpyP) derivative functionalized with a platinum(II) complex bearing long alkyl chains.

Results and Discussion

The synthetic route to the porphyrin platinum(II) complex [Pt(Lau$_2$dim)Me]$_4$(TpyP)(CF$_3$SO$_3$)$_4$ (**1**) (Lau$_2$dim = didodecyldiimine) can be summarized as follows (Scheme 1): (i) the diimine ligand Lau$_2$dim is readily prepared, according to a literature method,[15] by reacting dodecylamine and glyoxal in methanol; (ii) in analogy with a well-established procedure,[14] the diimine ligand is reacted with the complex *trans*-[Pt(Me$_2$SO)$_2$MeCl] in methanol, in the presence of a stoichiometric amount of AgCF$_3$SO$_3$; separation of solid AgCl and cautious evaporation of the excess solvent affords the sulfoxide complex [Pt(Lau$_2$dim)Me(Me$_2$SO)](CF$_3$SO$_3$); (iii) this latter compound is reacted with a stoichiometric amount of the TpyP porphyrin in chloroform leading almost quantitatively to the tetranuclear complex **1**. The gradual platination of the porphyrin can be monitored easily in situ by ^{1}H NMR spectroscopy, by titrating a solution of TpyP with the sulfoxide complex. The aromatic region of the spectrum shows a decrease of the signals for TpyP and a matching increase of the peaks due to intermediate mono-, di- and trisubstituted species, af-

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[a] Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica and ICTPN−CNR, Sezione di Messina - Università di Messina,
Salita Sperone, 31-Vill. S. Agata-98166 Messina, Italy
Fax: (internat.) +39-090/393-756
E-mail: monsu@chem.unime.it
[b] INFM, Unità di Messina
Salita Sperone, 31-Vill. S. Agata-98166 Messina, Italy

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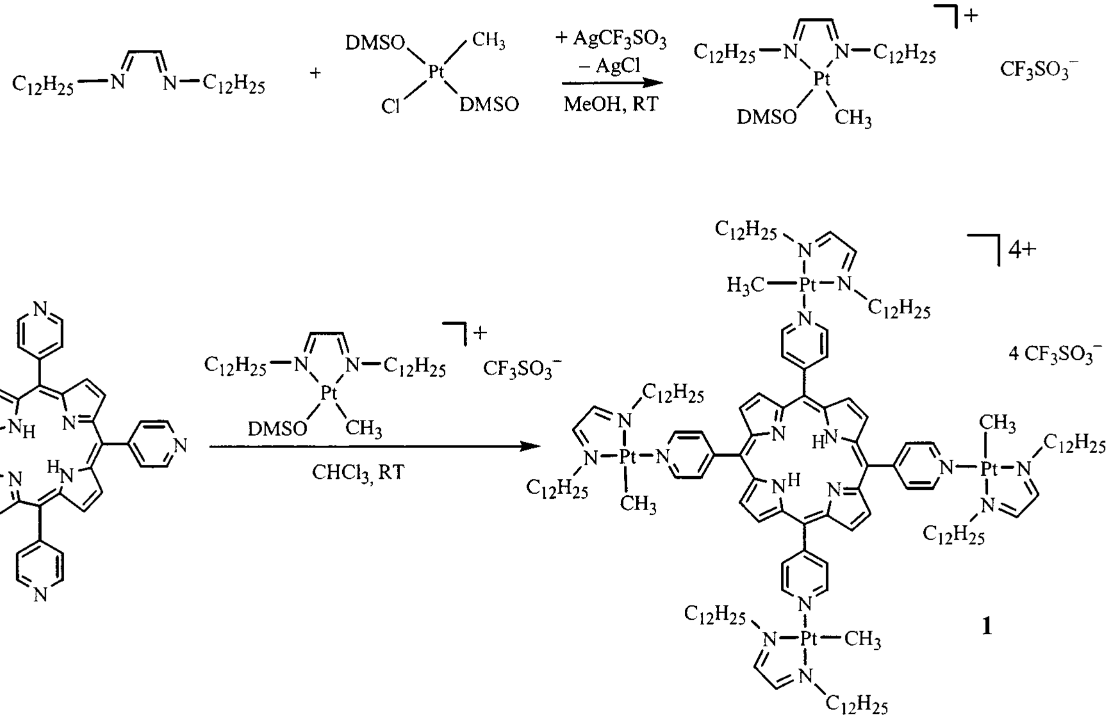

Scheme 1

fording eventually the required tetrasubstituted complex with a metal to porphyrin ratio of 4:1.

The UV/Vis electronic spectrum of **1** in acetone exhibits an intense Soret band at 422 nm ($\varepsilon = 2.76 \times 10^5\ \mathrm{M}^{-1}\mathrm{cm}^{-1}$), which is bathochromically shifted with respect to the free TpyP porphyrin ($\Delta\lambda = +9$ nm, Figure 1). A series of four Q-bands are present at longer wavelengths. The resonance light-scattering[17] spectrum of the acetone solution of **1** exhibits a rather low intensity with respect to the neat solvent, and is strongly modulated by the absorbance of the sample, suggesting the monomeric nature of this complex in acetone. The platinated porphyrin is still emissive in acetone solutions. The fluorescence spectra display the typical two-band emission at 654 and 716 nm, very similar (even if partially quenched by the heavy atom effect) to those of the parent porphyrin and of other tetraaryl-substituted porphyrins (inset of Figure 1).[18] The excitation spectra match the absorption spectra.

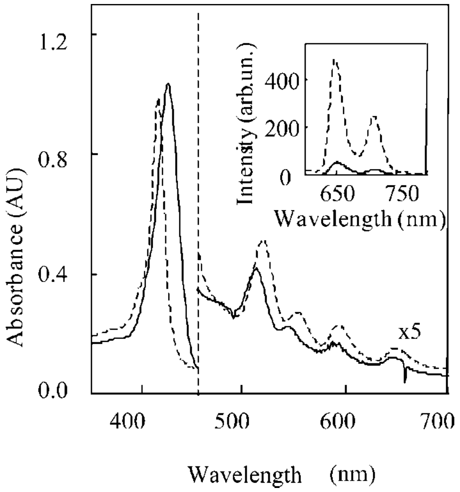

Figure 1. UV/Vis spectra of 5 μM solutions of TpyP (dashed line) and complex **1** (solid line) in acetone [the inset shows the fluorescence emission spectra of TpyP (dashed line) and complex **1** (solid line) in acetone ($\lambda_{exc} = 420$ nm; emissions are corrected for absorption)]

Chloroform or acetone solutions of complex **1** have been evaporated on glass cover slides. The resulting films exhibit an intense and sharp Soret band at 431 nm and the typical two-band emission fluorescence at 662 and 720 nm. Both the Soret and the emission features are bathochromically shifted with respect to the organic solution phase. These observations suggest a well-defined geometrical arrangement of porphyrins in the solid state, which could be accounted for by the occurrence of porphyrin−porphyrin interactions, in spite of the presence of the bulky alkyl side chains. These latter could be responsible for a further stabilization of the structure through hydrophobic interactions, which help to orientate the chromophore planes (Figure 2). Optical microscopy on these samples revealed a distribution of apparently globular objects, which are stable at 298 K for at least a week. After this period, the aggregates collapse in continuum unstructured layers. Scanning Electron Microscopy (SEM) has been exploited to investigate the morphology of this system. The SEM images (Figure 3) show a population of almost spherical aggregates with sizes spanning from 1000 up to 2000 nm. The presence of platinum in the aggregates is confirmed by Energy Dispersion Spectrometry (EDS), which shows the typical pattern of this element. The clear-cut evidence that compound **1** retains its identity in the globular aggregates has been proved by stripping the compound from the glass with acetone and comparing the UV/Vis absorption and fluorescence emission of these solutions with those of **1** in the same solvent prior to deposition. Analogous experiments performed using solutions of [Pt(Lau$_2$dim)Me(Me$_2$SO)](CF$_3$SO$_3$) or of the platinated porphyrin compound [Pt(Cy$_2$dim)Me]$_4$(T-pyP)(CF$_3$SO$_3$)$_4$ [13] resulted only in the formation of unstructured films, resembling a waxy layer.

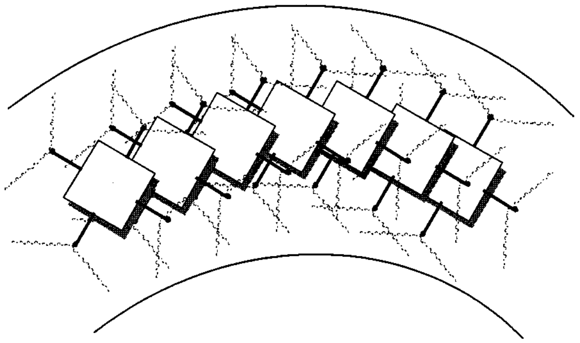

Figure 2. Schematic model for the arrangement of porphyrins in the aggregates

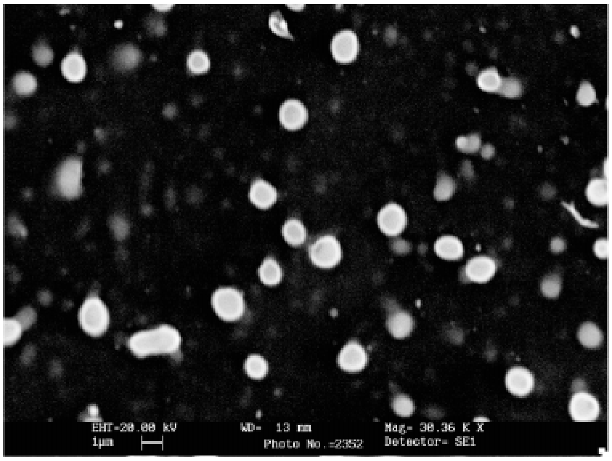

Figure 3. SEM image acquired on a sample of **1** deposited on glass from an acetone solution; the slide has been coated with graphite for EDS analysis

The growth of porphyrin wheels[10c] and of other well-defined patterns[19] of chromophores on different solid substrates has been explained on the basis of surface forces acting at the interface between the solid, the liquid and the gas phase. A similar mechanism could well apply to the growth of objects of spherical shape, even if a complete understanding deserves further investigations. The nature of the solvent does not allow a complete wettability of the glass substrate, leading to an increase of the contact angle. The droplets are pinned at the glass surface by the roughness of the surface or by defects present in the film. On evaporation the hydrophobic porphyrin concentrates in the droplet which tends to assume a spherical shape. The resulting structure should be stabilized by included solvent molecules. Further studies are in progress to test the catalytic ability of aggregated manganese(III) porphyrin derivatives in oxidative processes.

Experimental Section

General Procedures and Chemicals: All solvents were dried according to standard procedures by distillation under an oxygen-free nitrogen atmosphere from appropriate drying agents (i.e. dichloromethane from barium oxide and diethyl ether from sodium benzophenone ketyl). CDCl$_3$ was purchased from Cambridge Isotopes Laboratories (D, 99.8%). 5,10,15,20-tetrakis(4-pyridyl)-21*H*,23*H*-porphyrin (TpyP) was purchased from Aldrich. K$_2$PtCl$_4$ (Strem Chemical Co.) was purified from metallic Pt and K$_2$PtCl$_6$ by dissolving it in water and filtering. Tetramethyltin was received from Aldrich and its purity was checked by ^{1}H NMR spectroscopy. All the other reagents were of the highest commercial grade available and were used as received or were purified by distillation or recrystallization where necessary.

Instrumentation: ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 298 K on a Bruker AMX R-300 spectrometer operating with a broad-band probe at 300.13 and 75.7 MHz for ^{1}H and ^{13}C nuclei, respectively. Chemical shifts (δ, ppm) are referred to SiMe$_4$. UV/Vis spectra were measured on a Hewlett Packard mod. HP 8453 diode array spectrophotometer. Fluorescence and resonance light scattering experiments were performed on a Jasco mod. FP-750 spectrofluorimeter equipped with a Hamamatsu R928 PMT using, in this latter case, a synchronous scan protocol with a right-angle geometry.[17] Microanalysis was performed by Redox Analytical Laboratories, Milan, Italy. SEM was performed on a LEO S420 Cambridge instrument operating with an accelerating potential of 20 kV. The samples were prepared by graphite coating for the EDS analysis.

Lau$_2$dim: Didodecyldiimine (Lau$_2$dim) was prepared following a literature method used for other dialkyl diimines.[15] The solid compound was crystallized from methanol. Yield 75%. C$_{26}$H$_{52}$N$_2$ (392.7): calcd. C 79.51, H 13.36, N 7.14; found C 79.3, H 13.5, N 7.10. ^{1}H NMR (CDCl$_3$): $\delta = 7.9$ (s, 2 H), 3.55 (t, $^3J_{\mathrm{H-H}} = 6.9$ Hz, 4 H), 1.65 (m, 4 H), 1.24 (m, 36 H), 0.85 (t, $^3J_{\mathrm{H-H}} = 6.6$ Hz, 6 H). ^{13}C NMR (CDCl$_3$): $\delta = 162$ (CH), 61 (C$_1$-N), 32 (C$_2$-N), 30 (C$_3$-N), 29 (2C), 27 (3C), 22 (3C), 15 (CH$_3$). MS-EI: *m/z* = 391 [M − H$^+$]. M.p. 63 °C.

[Pt(Lau$_2$dim)Me(Me$_2$SO)](CF$_3$SO$_3$): The precursor [Pt(Lau$_2$dim)-Me(Me$_2$SO)](CF$_3$SO$_3$) was prepared using a slightly modified literature method.[14] A weighed amount of *trans*-[Pt(Me$_2$SO)$_2$MeCl][16] (40.2 mg, 0.1 mmol) was reacted in methanol (70 mL) with an equimolar amount of AgCF$_3$SO$_3$ and the ligand Lau$_2$dim. After stirring for 30 min, AgCl was removed by centrifugation. The solvents were then evaporated under reduced pressure, and the resulting yellow-orange solid was dissolved in dichloromethane and filtered through a cellulose column to remove residual AgCl. The compound was precipitated by adding diethyl ether and cooling to −30 °C. 58 mg of the complex were recovered. Yield 70%. C$_{30}$H$_{61}$F$_3$N$_2$O$_4$PtS$_2$ (830.0): calcd. C 43.41, H 7.41, N 3.37; found C 43.2, H 7.2, N 3.5. ^{1}H NMR (CDCl$_3$): $\delta = 8.87$ (s, $^3J_{\mathrm{Pt-H}} = 46$ Hz, 1 H), 8.84 (s, $^3J_{\mathrm{Pt-H}} = 83$ Hz, 1 H), 3.99 (t, 2 H), 3.77 (m, 2 H), 3.36 (s, $^3J_{\mathrm{Pt-H}} = 32$ Hz, 6 H), 1.67 (m, 4 H), 1.24 (m, 36 H), 0.87 (t, $^3J_{\mathrm{H-H}} = 6$ Hz, 6 H), 0.79 (s, $^2J_{\mathrm{Pt-H}} = 70.2$ Hz, 3 H). ^{13}C NMR (CDCl$_3$): $\delta = 173$ (CH), 166 (CH′), 120.4 ($^2J_{\mathrm{F-C}} = 320$ Hz, CF$_3$), 62.3, 59.3 (C$_2$ + C$_{2'}$), 45.5 ($^2J_{\mathrm{Pt-C}} = 84$ Hz, Me$_2$SO), 41, 40.5 ($C_3 + C_{3'}$), 32−26.22 (18 C), 14 ($C_{12} + C_{12'}$), −9.6 ($^1J_{Pt-C}$ = 700 Hz, CH_3). MS-FAB: m/z = 680 [$M^+ - CF_3SO_3$].

[Pt(Lau$_2$dim)Me]$_4$(TpyP)(CF$_3$SO$_3$)$_4$ (1): [Pt(Lau$_2$dim)Me(Me$_2$SO)](CF$_3$SO$_3$) (54 mg, 0.064 mmol) was added to a stirred solution of TpyP (10 mg, 0.016 mmol) in 25 mL of freshly distilled chloroform. The solution was allowed to react for 2 hours, and the solvent was then removed under reduced pressure. The resulting deep purple compound was dissolved in acetone and precipitated by adding diethyl ether and cooling to −30 °C (46 mg). Yield 80%. $C_{152}H_{246}F_{12}N_{16}O_{12}Pt_4S_4$ (3626.3): calcd. C 50.35, H 6.84, N 6.18; found C 50.01, H 6.50, N5.98. ^{1}H NMR (CDCl$_3$): δ = 9.14 (m, $^3J_{H-H}$ = 5.5 Hz, 8 H), 8.97 (s, 8 H), 8.85 (s, 4 H), 8.71 (s, 4 H), 8.45 (m, $^3J_{H-H}$ = 5.5 Hz, 8 H), 3.99 (m, 8 H), 3.85 (m, 8 H), 1.85−1.05 (m, 160 H), 0.86 (m, $^3J_{H-H}$ = 6 Hz, 24 H), 0.60 (s, 12 H), −3.00 (s, 2 H). MS (MALDI-TOF): m/z = 1972 [M − 2Pt − $CF_3SO_3^+$], 1220.8 [M − 3Pt − $CF_3SO_3^+$]. UV/Vis (acetone): λ_{max} (ε) = 422 (276000), 514, 550, 592, 648 nm. UV/Vis (on glass): λ_{max} = 431, 521, 555, 598, 650 nm. Fluorescence emission (acetone): λ_{exc} = 420 nm; λ_{em} = 654, 716 nm. Fluorescence emission (on glass): λ_{exc} = 420 nm; λ_{em} = 662, 720 nm.

Deposition on Glass: Microscope slides, cleaned prior to use by immersion in a 1:1 mixture of concentrated NH_3 solution and 30+% H_2O_2, then rinsed with Milli-Q water and dried under a steam of N_2, were used as film substrates. A droplet of a 10^{-5}−10^{-4} M solution of **1** in acetone or chloroform (Aldrich, Spectral grade) was placed on the substrate and evaporation was achieved by gentle spinning at 298 K.

Supporting Information Available (see footnote on the first page of this article): ^{1}H NMR titration of TpyP with the precursor platinum(II) complex (Figure S1), UV/Vis and fluorescence emission of **1** in acetone solution and on glass surface (Figure S2 and S3), optical images (1000× magnification) of different porphyrin complexes (Figure S4) and Energy Dispersion Spectrometry (EDS) profile on samples of **1** deposited on glass (Figure S5).

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[1] [1a] J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**. [1b] J.-H. Fuhrhop, J. Koning, *Membranes and Molecular Assemblies: The Synkinetic Approach* (Ed.: J. F. Stoddart), RSC, **1994**.

[2] W. I. White, in *The Porphyrins* (Ed.: D. Dolphin), Academic Press, New York, **1978**, vol. 5, Chapter 7.

[3] [3a] K. M. Kadish, B. G. Maiya, C. Araullo-McAdams, *J. Phys. Chem.* **1991**, *95*, 427−431. [3b] K. M. Kadish, B. G. Maiya, C. Araullo-McAdams R. Guilard, *Inorg. Chem.* **1989**, *28*, 2725−2731. [3c] S. Mazumdar, *J. Phys. Chem.* **1990**, *94*, 5947−5949. [3d] M. J. Minch, G. La Mar, *J. Phys. Chem.* **1982**, *86*, 1400−1406.

[4] [4a] A. P. H. J. Schenning, J. H. Lutje Spelberg, D. H. W. Hubert, M. C. Feiters, R. J. M. Nolte, *Chem. Eur. J.* **1998**, *4*, 871−880. [4b] D. Mansuy, M. Fontecave, J.-F. Bartoli, *J. Chem. Soc., Chem. Commun.* **1983**, 253−254. [4c] A. M. d′ A. Rocha Gonsalves, R. A. W. Johnstone, M. M. Pereira, J. Shaw, A. J. F. do N. Sobral, *Tetrahedron Lett.* **1991**, *32*, 1355−1358. [4d] J. T. Groves, R. Neumann, *J. Am. Chem. Soc.* **1987**, *109*, 5045−5047.

[5] R. Guilard, N. Senglet, Y. H. Liu, D. Sazou, E. Findsen, D. Faure, T. Des Courieres, K. M. Kadish, *Inorg. Chem.* **1991**, *30*, 1898−1905.

[6] [6a] J.-H. Fuhrhop, C. Demoulin, C. Bottcher, J. Koning, U. Siggel, *J. Am. Chem. Soc.* **1992**, *114*, 4159−4165. [6b] J.-H. Fuhrhop, C. Demoulin, C. Bottcher, J. Koning, U. Siggel, *J. Am. Chem. Soc.* **1993**, *115*, 11036−11037. [6c] J.-H. Fuhrhop, U. Bindig, U. Siggel, *J. Chem. Soc., Chem. Commun.* **1994**, 1583−1584.

[7] T. Komatsu, E. Tsuchida, C. Bottcher, D. Donner, C. Messerschmidt, U. Siggel, W. Stocker, J. P. Rabe, J.-H. Fuhrhop, *J. Am. Chem. Soc.* **1997**, *119*, 11660−11665.

[8] T. Komatsu, K. Nakao, H. Nishide, E. Tsuchida, *J. Chem. Soc., Chem. Commun.* **1993**, 728−730.

[9] E. Tsuchida, T. Komatsu, K. Arai, H. Nishide, *J. Chem. Soc., Chem. Commun.* **1993**, 730−732.

[10] [10a] A. P. H. J. Schenning, F. B. G. Benneker, H. P. M. Geurts, X. Y. Liu, R. J. M. Nolte, *J. Am. Chem. Soc.* **1996**, *118*, 8549−8552. [10b] J. Hofkens, L. Latterini, P. Vanoppen, H. Faes, K. Jeuris, S. Defeyter, J. Kerimo, P. F. Barbara, F. C. Deschryver, A. E. Rowan, R. J. M. Nolte, *J. Phys. Chem. B* **1997**, *101*, 10588−10598. [10c] L. Latterini, R. Blossey, J. Hofkens, P. Vanoppen, F. C. Deschryver, A. E. Rowan, R. J. M. Nolte, *Langmuir* **1999**, *15*, 3582−3588.

[11] W. T. S. Huck, A. Rohrer, A. T. Anilkumar, R. H. Fokkens, N. M. M. Nibbering, F. C. J. M. van Veggel, D. N. Reinhoudt, *New J. Chem.* **1998**, *22*, 165−168.

[12] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853−908.

[13] L. Monsù Scolaro, C. Donato, M. Castriciano, A. Romeo, R. Romeo, *Inorg. Chim. Acta* **2000**, *300−302*, 978−986.

[14] R. Romeo, L. Monsù Scolaro, N. Nastasi, G. Arena, *Inorg. Chem.* **1996**, *35*, 5087−5096.

[15] J. M. Kliegman, R. K. Barnes, *Tetrahedron* **1970**, *26*, 2555−2560.

[16] R. Romeo, L. Monsù Scolaro, *Inorg. Synth.* **1998**, *32*, 153−158.

[17] R. F. Pasternack, P. J. Collings, *Science* **1995**, *269*, 935−939.

[18] K. Kalyanasundaram, *Inorg. Chem.* **1984**, *32*, 2453−2459.

[19] C. J. Brinker, Y. F. Lu, A. Sellinger, H. Y. Fan, *Adv. Mater.* **1999**, *11*, 579−585.

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