Porphyrin Deposition Induced by UV Irradiation

Luigi Monsù Scolaro,*,[†,‡,§] Andrea Romeo,[†,‡] Maria Angela Castriciano,[†] Giovanna De Luca,[†]
Salvatore Patanè,[‡,||] and Norberto Micali[⊥]

*Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina,
Salita Sperone 31, 98166 Vill.S.Agata, Messina, Italy, INFM, Unità di Messina, Messina, Italy, ISMN-CNR,
Sezione di Messina, Messina, Italy, Dipartimento di Metodologie Fisiche Avanzate, Università di Messina,
Messina, Italy, and IPCF-CNR, Istituto per i Processi Chimico-Fisici, Sezione di Messina, Via La Farina 237,
98123, Messina, Italy*

Received October 29, 2002 ; E-mail: monsu@chem.unime.it

The remarkable recent progress in nanotechnology is mainly due to the ability to synthesize, investigate, and exploit materials with structural modulation on the nanometer scale. In this respect, several methodologies have been developed to realize well-defined patterns on the nano- and mesoscopic scales.[1,2] Nanostructures display unusual optical and optoelectronic properties, often quite different with respect to single molecules and the bulk material.[3] Porphyrins are attractive compounds because they are relatively easy to synthesize and their photophysical properties can be tuned through careful choice of peripheral substituents and inserted metal ions.[4,5] Many thin film structures, such as Langmuir−Blodgett (LB) films,[6] self-assembled monolayers (SAMs),[7] and evaporated films of porphyrin wheels,[8] have been reported.

As part of our research program on the aggregation behavior of this class of compounds, we have focused on homo- and hetero-aggregated species formed by various water-soluble porphyrins.[9] The porphyrin tetra(4-pyridyl)porphine (TpyP, hereafter) is insoluble in aqueous solution, but it is readily soluble under acidic conditions, and the X-ray structure of its fully protonated form has been reported.[10] Its photophysical properties as monomer in organic solvents have been investigated,[11,12] while a report on its aggregation behavior in mixed organic-aqueous media pointed out the elusive nature of the aggregates.[13]

Here we describe a simple method to deposit aggregates of acid TpyP having sizes from hundreds of nanometers up to tenths of microns from a chlorinated solvent solution on a silica surface.

After repetitive scanning with a diode-array spectrophotometer in a solution of TpyP (∼10^{-5} M) in CH_2Cl_2,[14] the strong Soret band at 417 nm gradually decreases in intensity, whereas a new broad feature increases at about 485 nm. The Q-bands of the TpyP porphyrin at 513, 546, 588, and 648 nm undergo a red shift, and at the end of the process only two are clearly detectable and located at 625 and 670 nm. The fluorescence spectra of the starting solution provide evidence for the typical two band emission of this compound,[11] while it is almost completely quenched when the 485 nm species is formed. The corresponding resonance light-scattering (RLS)[15] spectra performed on the final solution reveal the occurrence of extended porphyrin aggregates, as evidenced by a large red-shifted enhancement of the scattered light at 530 nm, with respect to the intensity profile of an untreated sample. The deep well at 440 nm can be ascribed to photon loss due to absorption, and, in agreement with previous spectral investigations,[12] it suggests the presence in solution of diacid H_6TpyP^{6+}. On removing the silica
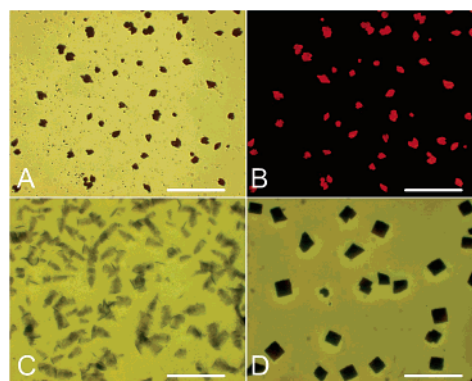
Figure 1. Optical images of samples deposited on silica obtained by irradiating porphyrin solutions in CH_2Cl_2 ([porph] = 10^{-5} M; delay time 5 s; total time 3600 s). (A) TpyP(4) transmission, (B) TpyP(4) fluorescence mode exciting at 532 nm, (C) Zn(II)TpyP(4), and (D) Mn(III)TpyP(4) (the bar is 50 μm).

cell containing the solution from the spectrophotometer compartment, we found that it is possible to observe on the wall exposed to the light beam the presence of a red-brownish spot, which, after removing the solution and drying, has been analyzed. A comparison of spectroscopic features allowed us to assign this deposit to the porphyrin with only the meso pyridyl substituent groups protonated, $(H_4TpyP^{4+})4Cl^-$. Interestingly, while the fluorescence emission of the aggregated $(H_6TpyP^{6+})6Cl^-$ formed in the bulk solution is almost completely quenched, the deposited $(H_4TpyP^{4+})4Cl^-$ porphyrin is emissive.

This phenomenon is not limited to TpyP porphyrin, but it is operative also in the case of its Mn(III) and Zn(II) metal derivatives. An analysis of the spots obtained with these compounds has been performed by optical microscopy (Figure 1).

In the case of TpyP, a population of aggregates is evident with sizes on the order of 1 μm. SEM analysis of these samples evidenced the presence of geminate crystals. Well-defined crystals are formed in the case of the Mn(III) derivative (size range 1−10 μm), while needle crystals, from which a ribbonlike structure grows in solution, are present in the case of the Zn(II) derivative. A possible explanation for the observed different morphology can be found in the difference of the coordination environment for the two metal ions. Formation of face-to-face geometries by π−π stacking interactions is prevented by two axial ligands in the Mn-(III) complex (six-coordinated), while this possibility remains operative in the case of the Zn(II) complex (five-coordinated), in which a face of the porphyrin ligand is still available for the interaction with a neighboring porphyrin. The deposition of metal derivatives rules out the involvement of the protonated nitrogen
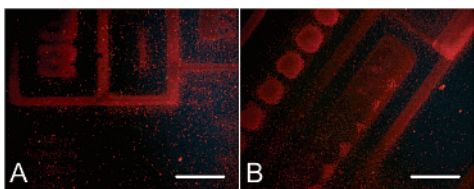
Figure 2. Optical image of the patterning of a cuvette silica wall with TpyP irradiating UV light through a micromask (fluorescence detection). The bar is 100 μm.
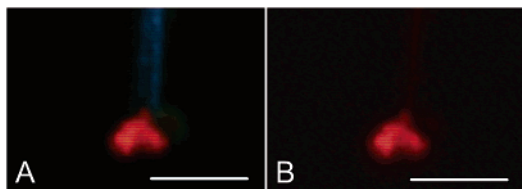

Figure 3. Optical images of the nanocrystal grown on the tip of a SNOM optical probe: (A) fluorescence field visualization, (B) fluorescence emission from the nanocrystal (excitation at 532 nm through the fiber). The bar is 10 μm.

core in the formation of the aggregated species. Indeed, Akins et al. showed that the addition of 10 vol % trifluoroacetic acid to a solution of TpyP in dichloromethane yields a species with a Soret band at 440 nm, which was assigned to the monomeric diacid H_6-$TpyP^{6+}$.[12] This finding suggests that an important role in driving the aggregation should be played by ion-pairing with the chloride anion.

The formation of crystals by UV light irradiation has been already reported in the case of chloroform solutions of strychnine, leading to well-defined macroscopic crystals of the acid form which precipitated from the solution.[16] The mechanism of deposition for the reported porphyrins can be explained through the decomposition of the halogenated solvent as induced by UV irradiation.[17] Hydrochloric acid is generated at the interface between the light-exposed silica wall and the bulk solvent. Rapid protonation of the porphyrin and consequent formation of initial seeds on the silica surface determine the growth of the observed mesostructures. In this respect, a significant role is played by the total irradiation time and by the cycling time. To grow well-defined structures on the silica substrate, the amount of hydrochloric acid should be kept quite low. Accordingly, a higher light flux leads to diffusion of the acid into the bulk solution, causing the aggregated porphyrin to form and precipitate not in contact with the exposed surface. The role of the triplet excited state of benzene in the decomposition of chloroform on irradiating at 254 and 313 nm has already been addressed.[18] To exclude the role of porphyrin as a sensitizer for the photodecomposition of dichloromethane, a series of blank experiments have been performed irradiating the neat solvent.[19] After the light exposure, the formation of acid has been easily proved by adding small quantities of free base TpyP, which turns to the characteristic green color of its diacid form.

This method has been successfully applied to pattern a silica surface with porphyrins using a mask commonly used for microlithography. Irradiation of a solution of TpyP in dichloromethane placing the mask between the UV source and the target surface leads to the formation of well-defined fluorescent porphyrin deposits (Figure 2).[20]

Another interesting application consists of growing porphyrin mesoscopic crystals on the tip of a SNOM optical fiber (~50 nm

of optical aperture).[21] Figure 3a show a tip on which the porphyrin nanocrystal is clearly evident. The fluorescence of the crystal can be also excited by coupling the fiber with the 532 nm line of a 10 mW Nd:YAG laser (Figure 3b). This property can be properly exploited to build nano- or microprobes to be used, for example, for microscopy applications.

In conclusion, a very simple and convenient method to deposit porphyrin aggregates and crystals from halogenated solvents on silica substrate has been developed. The possibility of tuning the photophysical properties of the mesoaggregates on changing the metal ions or the substituents on the porphyrins opens the way to different potential applications, for example, in the field of electrooptical devices. Further investigations and developments are currently underway.

Supporting Information Available: Spectroscopic investigations in bulk solution and on silica surface (UV/vis, fluorescence, and RLS spectra) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Wallraff, G. M.; Hinsberg, W. D. *Chem. Rev.* **1999**, *99*, 1801−1821.
(2) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823−1848.
(3) Bawendi, M. C.; Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477.
(4) Pasternack, R. F.; Gibbs, E. J. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 1996; Vol. 33, pp 367−397.
(5) White, W. I. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 5, p 303.
(6) Kroon, J. M.; Sudholter, E. J. R.; Schenning, A. P. H. J.; Nolte, R. J. M. *Langmuir* **1995**, *11*, 214−220.
(7) Zhang, Z.; Hou, S.; Zhu, Z.; Liu, Z. *Langmuir* **2000**, *16*, 537−540.
(8) Schenning, A. P. H. J.; Benneker, F. B. G.; Geurts, H. P. M.; Liu, X. Y.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1996**, *118*, 8549. Hofkens, J.; Latterini, L.; Vanoppen, P.; Faes, H.; Jeuris, K.; Defeyter, S.; Kerimo, J.; Barbara, P. F.; Deschryver, F. C.; Rowan, A. E.; Nolte, R. J. M. *J. Phys. Chem. B* **1997**, *101*, 10588. Latterini, L.; Blossey, R.; Hofkens, J.; Vanoppen, P.; Deschryver, F. C.; Rowan, A. E.; Nolte, R. J. M. *Langmuir* **1999**, *15*, 3582−3588.
(9) Mallamace, F.; Micali, N.; Trusso, S.; Monsù Scolaro, L.; Romeo, A.; Terracina, A.; Pasternack, R. F. *Phys. Rev. Lett.* **1996**, *76*, 4741. Mallamace, F.; Monsù Scolaro, L.; Romeo, A.; Micali, N. *Phys. Rev. Lett.* **1999**, *59*, 3480. Micali, N.; Mallamace, F.; Romeo, A.; Purrello, R.; Monsù Scolaro, L. *J. Phys. Chem. B* **2000**, *104*, 5897. Micali, N.; Romeo, A.; Lauceri, R.; Purrello, R.; Mallamace, F.; Monsù Scolaro, L. *J. Phys. Chem. B* **2000**, *104*, 9416.
(10) Stone, A.; Fleischer, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 2734.
(11) Kalyanasundaram, K. *Inorg. Chem.* **1984**, *32*, 2453−2459.
(12) Akins, D. L.; Zhu, H. R.; Guo, C. *J. Phys. Chem.* **1996**, *100*, 5420−5425.
(13) Khairutdinov, R. F.; Serpone, N. *J. Phys. Chem. B* **1999**, *103*, 761−769.
(14) A porphyrin solution (10^{-5} M) placed in a silica cell was irradiated by repetitive scanning (1 s) every 5 s for a total time of 3600 s. Changes in the total time irradiation change the size of the nanocrystals.
(15) Pasternack, R. F.; Collings, P. J. *Science* **1995**, *269*, 935.
(16) Turkovic, I. *J. Pharm. Belg.* **1976**, *31*, 277−286.
(17) $CHCl_3$ and CCl_4 gave the same results, whereas DMSO, MeOH, and DMF were not effective, proving the role of HCl.
(18) Semeluk, G. P.; Unger, I. *Nature* **1963**, *198*, 853−855. Ng, S. H.; Semeluk, G. P.; Unger, I. *Can. J. Chem.* **1968**, *46*, 2459−2461
(19) The solvent, placed in a 1 cm path length silica cell, was irradiated 300 s by an unfiltered 20 W deuterium lamp or by using the 352 nm line of a 10 mW He/Cd laser.
(20) Patterning was obtained by irradiating for 30 s the porphyrin solution (10^{-5} M in CH_2Cl_2) with a Xe lamp (75 W) placed at 50 cm. A micropatterned mask was placed between the UV source and the target.
(21) An Al-coated SNOM silica optical fiber (50 nm optical aperture) was coupled with the 352 nm line of a 10 mW He/Cd laser, and the tip was immersed into a porphyrin solution in dichloromethane (10^{-5} M). The irradiation was performed continuously for 1 h. After it was rinsed with CH_2Cl_2 to remove the porphyrin excess, the tip was observed through an optical microscope in fluorescence mode (excitation green filter).

JA029134Y