DOI: 10.1002/ejoc.200801300

Redox- and pH-Controlled Mechanized Nanoparticles

Niveen M. Khashab,[a] Ali Trabolsi,[a] Yuen A. Lau,[b] Michael W. Ambrogio,[a] Douglas C. Friedman,[a] Hussam A. Khatib,[a] Jeffrey I. Zink,*[b] and J. Fraser Stoddart*[a]

Dedicated to Professor Alain Krief

Keywords: Ferrocene / Nanoparticles / Cucurbit[7]uril / β-Cyclodextrin / Redox chemistry

A new class of mechanized silica nanoparticles, which exploits the stability of the inclusion complexes formed between ferrocenedicarboxylic acid and both cucurbit[7]uril (CB7) and β-cyclodextrin (β-CD), are described. Mesoporous silica nanoparticles, capable of storing a payload of small molecules and releasing it following particular activation processes, have been designed and decorated with ferrocenecarboxylic acid stalks. The storage and release of the payload is controlled by the host–guest interaction between the ferrocene moiety (guest) and the ring moiety (CB7 or β-CD). Ferrocene-based Mechanized NanoParticles (FMNPs) were efficiently prepared, loaded with Rhodamine dye, and then tested under different activation procedures. The systems operated successfully under redox control (oxidation of ferrocenedicarboxylic acid) in the presence of β-CD and under pH control (deprotonation of ferrocenedicarboxylic acid pH > 4) in the presence of CB7.

Introduction

The ability to control the release of molecules from mesoporous silica nanoparticles promises to have far-reaching consequences for drug-delivery applications.[1] Both molecular and supramolecular nanovalves, which regulate the release of guest molecules from the nanopores of mesostructured silica nanoparticles, and operate under a range of stimuli, including pH,[2,3] competitive binding,[3] light,[4] and redox control,[5] have been designed and their successful operations demonstrated.[6] These systems are based on the switching of components that have been tethered to nanoparticle surfaces, such that access to the entrances of the nanopores can be opened and closed on demand. Mesoporous silica nanoparticles functionalized with molecular switches,[7] with a moving component able to block or expose the entrance to a pore orifice, and which operate to regulate the release of encapsulated molecules in a controlled manner, are promising vehicles for drug delivery because they are biologically compatible and are capable of storing and releasing molecules on demand. Although ferrocene switches have been widely reported in the literature,[8] no mechanized application has been reported. Herein, we describe Ferrocene-based Mechanized NanoParticles (FMNPs) that operate in water under redox or pH control, depending on the ring component blocking the pore, β-cyclodextrin (β-CD) for redox control or cucurbit[7]uril (CB7) for pH control.

Ferrocene (Fc) has captured the interest of chemists, leading to the formation of countless derivatives with applications in areas as diverse as catalysis,[9] nonlinear optics,[10] electrochemistry,[11] medicine and biology.[12] Recently, macromolecular derivatives with luminescent properties have been produced, with promising applications in the biosciences.[13] Polymers and dendrimers containing ferrocene units, either on their side chains or in their main chains, have also attracted increasing attention as they may feature new electrical, optical, or even magnetic properties.[14] Moreover, hydroxyferrocifen compounds, analogues to the anticancer drug Tamoxifen®, are a promising class of ferrocifen-type breast-cancer drug candidates, as they possess both endocrine-modulating properties and cytotoxic activity.[15]

Cyclodextrins (CDs) are amongst the most important and widely studied examples[16] of host molecules capable of forming inclusion complexes with a variety of guests – by incorporating them within the relatively nonpolar cavities of these cyclic oligosaccharides. Previous studies[16c] have emphasized the effect of cyclodextrins on the oxidation/reduction reactions of guest molecules and their use as modifiers of organic electrode reactions. The binding in-

---

[a] Department of Chemistry, Northwestern University,
2145 Sheridan Road, Evanston, IL 60208, USA
E-mail: stoddart@northwestern.edu
[b] Department of Chemistry and Biochemistry and California NanoSystems Institute, University of California – Los Angeles,
405 Hilgard Avenue, Los Angeles, CA 90095, USA
E-mail: zink@chem.ucla.edu

Supporting information for this article is available on the WWW under http://www.eurjoc.org/ or from the author.

teractions between β-CD and ferrocene derivatives[17] – including a ferrocenylalkyl disulfide[18a] and 7-ferrocenyl-2,4,6-heptatrienal[18b] – have been investigated extensively. In general, ferrocene residues are complexed to β-CD, whereas the oxidized, positively charged ferrocenium ions do not form stable complexes.[19,20] The family of cucurbiturils[20] is also well known for its host–guest interactions. In particular, CB7 forms stable inclusion complexes with both oxidation states of ferrocene, although the oxidized ferrocenium form is more strongly bound than the neutral form.[15b,21] Stable inclusion complexes with CB7 have binding constants in the 10^9–10^{13} range for neutral and cationic ferrocene guests. The anionic ferrocenecarboxylates, however, are not bound at all by CB7. Whereas the inclusion complexation of the surveyed guests inside β-CD seems to be controlled by the hydrophobic character of the ferrocene residue, their interactions with CB7 are pH-related.[22,23]

Results and Discussion

Mesoporous silica nanoparticles were prepared and treated with (3-aminopropyl)triethoxysilane (3-APTES) in order to achieve an amine-modified surface according to a published protocol.[7b] Ferrocenedicarboxylic acid was coupled with the amino-functionalized nanoparticles in DMF and then stirred at room temperature overnight. Water was added to quench the reaction, followed by an aqueous solution of Rhodamine dye. The nanoparticles were then stirred in an aqueous solution of Rhodamine B (RhB) dye for 48 h to allow the maximum amount of dye particles to diffuse into the silica pores. An excess of β-CD in H_2O was then added to the reaction mixture, which was left standing for 2 d to ensure the capping or proper binding of β-CD to ferrocene (Figure 1). The nanoparticles were then filtered and washed extensively with H_2O and MeOH to afford β-CD-capped MNPs. Substituting CB7 for β-CD in the last step, followed by repeated washing with an acidic aqueous MeOH solution, afforded CB7-capped MNPs (Figure 1). The ferrocene systems were characterized (see Supporting Information) by IR spectroscopy and SEM.

The interactions between β-CD and ferrocene complexes are very well established in the literature.[16c,16m,16n,16r,17] By contrast, the interaction of CB7 and ferrocene compounds under different pH conditions has been studied in less detail. Thus, the dependence on pH of CB7 binding towards ferrocenedicarboxylic acid was investigated (Figure 2) by ^{1}H NMR spectroscopy. At pH = 2, CB7 binds the protonated neutral ferrocenedicarboxylic acid as illustrated by an upfield shift of the resonances for the ferrocene protons. The resonances associated with CB7 remain relatively unchanged with respect to their chemical shifts upon complexation with ferrocenedicarboxylic acid. The static nature of

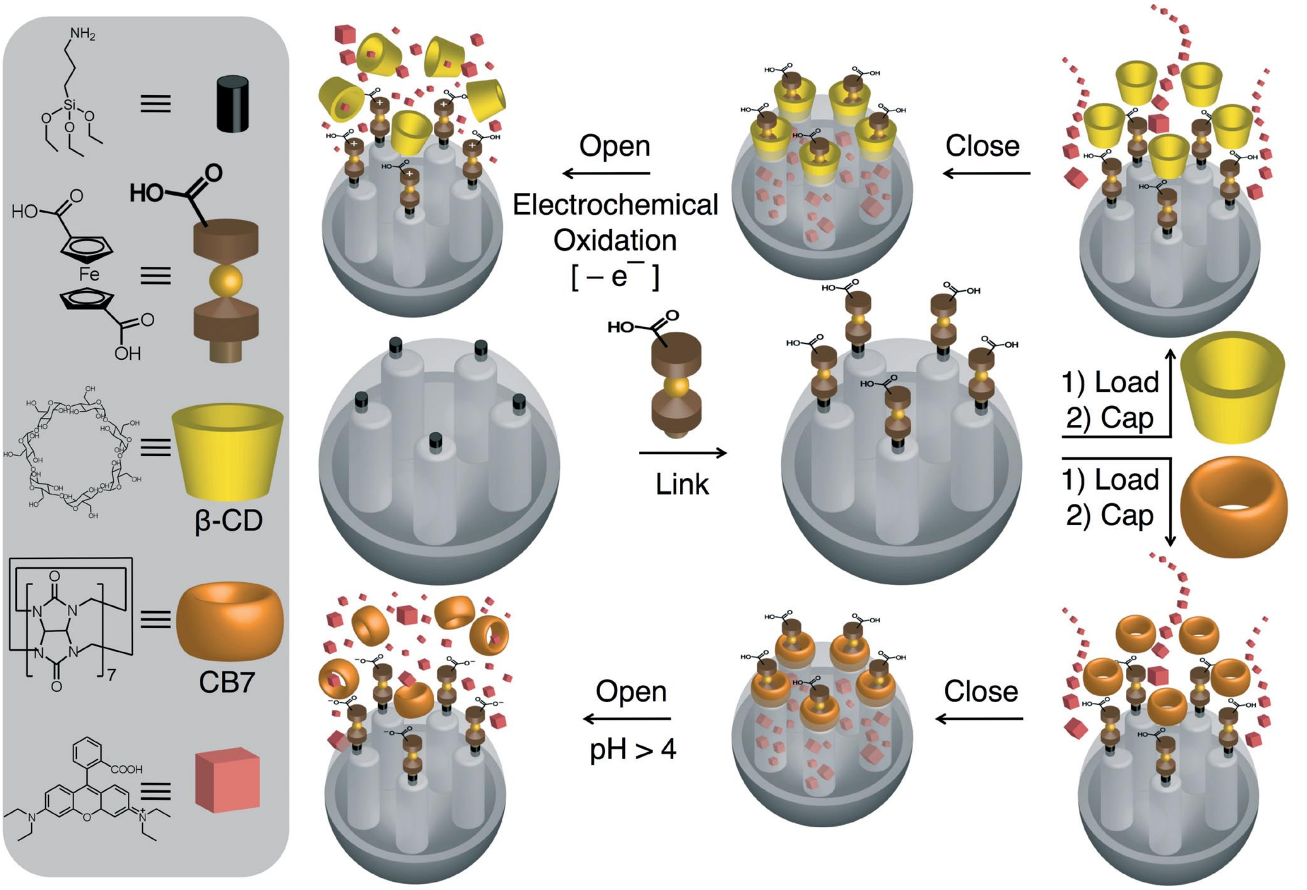

Figure 1. Design and preparation of FMNPs, which operate under redox or pH control according to the nature of the ring (β-CD in the top route and CB7 in the bottom route) capping the pores.

bound CB7 is consistent with recent literature precedent.[22] Increasing the pH to 10 yields the ferrocene dianion, which does not bind to the electron-rich interior of CB7. The appearance of free Fc peaks at δ = 4.80 and 4.56 ppm and the complete disappearance of the complexed ferrocene peaks at δ = 4.64 and 4.29 ppm show the complete dissociation from CB7.

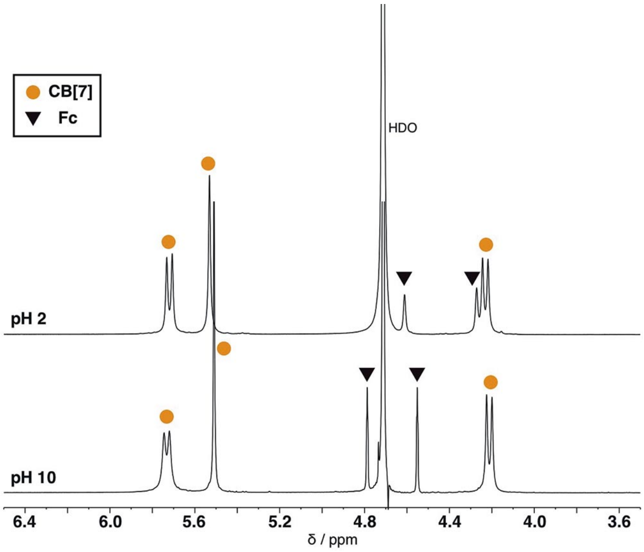

Figure 2. ^{1}H NMR spectra of ferrocenedicarboxylic acid (Fc) and cucurbit[7]uril (CB7) in D_2O solution (10 mM phosphate, 20% [D_4]-DMF). At pH = 2, the resonances associated with Fc exhibit upfield shifts characteristic[22] of bound CB7 guests. At pH = 10, the Fc^{2-} resonances remain in their original downfield positions, indicating no significant interactions with CB7.

The host–guest interactions between the ferrocene unit and the two ring types (β-CD and CB7) used in our investigations were also examined by cyclic voltammetry (see Supporting Information). The voltammetric behavior of the ferrocene thread was characterized by a reversible oxidation of its ferrocene unit. The effect of β-CD and CB7 on the cyclic voltammetric behavior of ferrocene was recorded and is shown in Figures S5, S6, and S7. The presence of 1 equiv. of β-CD resulted in an anodic shift (ca. 50 mV) in the position of the $E_{1/2}$ value for the oxidation of the ferrocene residue (Figure S5). This shift is characteristic of the formation of a stable inclusion complex between the β-CD and the ferrocene unit. Moreover, the presence of 1 equiv. of CB7 induces a more pronounced anodic shift (ca. 100 mV) in the position of the $E_{1/2}$ value for the oxidation of the carboxylic ferrocene residue, reflecting (Figure S6) a high binding between the ferrocene residue and the CB7. In strong contrast with the results recorded with the carboxylic ferrocene, the presence of CB7 has no effect on the voltammetric response of the anionic derivative of the ferrocene residue. The lack of host–guest interactions between CB7 and ferrocenecarboxylate can be attributed to the strong electrostatic repulsions between the carboxylate anion of the guest and the carbonyl oxygen atoms on the host portal.

The redox- and pH-triggered release of cargo molecules were monitored by using luminescence spectroscopy (see Supporting Information for experimental details). In both cases, the dye-loaded, β-CD- and CB7-capped nanoparticles (5 mg/mL) were placed in the corner of a cuvette before changing the pH of the solution or applying a voltage. In order to open the β-CD-capped nanoparticles, electrochemistry was coupled to luminescence spectroscopy. The oxidation of the ferrocence unit in H_2O (0.1 M NaCl used as supporting electrolyte) was performed electrochemically (see Supporting Information) by applying a voltage (1 V). The experiment was carried out in a custom-built optically transparent electrochemical cell by using a platinum (Pt) grid as the working electrode, a Pt wire as the counter electrode and an Ag wire as pseudo-reference electrode. To ensure the maximum contact of the nanoparticles with the Pt grid, the solution was stirred slowly.[24] Oxidation of the ferrocene unit initiates the dissociation of the inclusion complex Fc⊂β-CD and leads to the release of the dye particles from the pores. The fluorescence emission of the Rhodamine B was measured[24] by using a 530 nm excitation wavelength both before (V = 0 V) and after oxidation (V = 1 V) of the ferrocene unit (Figure 3). For the CB7-capped particles, the release of the trapped Rhodamine B molecules occurs under pH control. Deprotonation of the terminal carboxylic group induces strong electrostatic repulsions between the carboxylate group of the guest and the carbonyl oxygen atoms surrounding the host portals, and militates against any host–guest interactions between CB7 and the ferrocenecarboxylate unit. The dye-loaded, CB7-capped MNPs (10 mg) were placed in a corner of a cuvette before carefully adding a trifluoroacetic acid (TFA) solution (pH ≈ 3). The emission of RhB in the solution above the particles was measured as a function of time by using a 514 nm probe beam (25 mW) to excite the dye molecules as they

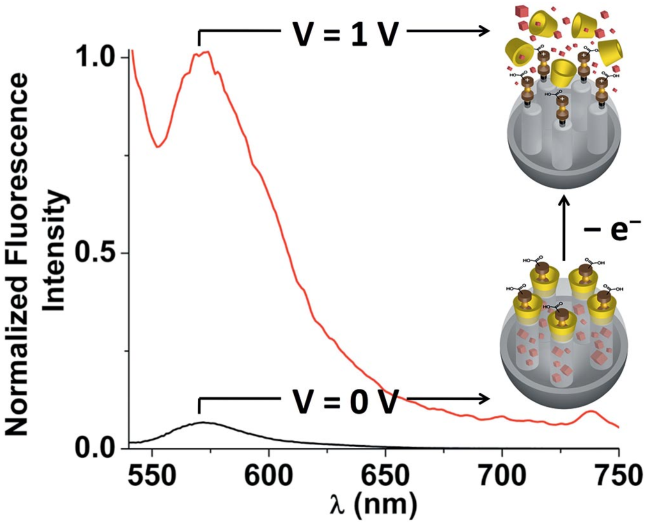

Figure 3. Emission spectrum showing the controlled release of Rhodamine B under redox conditions, in aqueous solution (0.1 M NaCl) at room temperature and by using a 530 nm excitation wavelength. The black spectrum (t = 0 min) was recorded at V = 0 V, and the red spectrum was recorded after applying 1 V for 400 min.

are released from the nanoparticles, both before and after the addition of 1 N NaOH. The RhB emission spectrum was recorded as a function of time at 1 s intervals. The release profile (Figure 4) was obtained by plotting the luminescence intensities of RhB at the emission maxima (578–582 nm) as a function of time. Prior to the addition of 1 N NaOH solution, the CB7-capped system was left in a pH = 3 TFA solution, and luminescence intensities of RhB were monitored. The system exhibited limited leakage, as indicated by the modest slope in the luminescence intensity. After changing the pH to 10, the emission intensity asymptotically approaches its maximum with a half-life value of about 100 min. The MNPs were further tested by measuring the emission of Rhodamine B in the solution above the nanoparticles using a 530 nm excitation wavelength (Figure S8 in the Supporting Information) before and after addition of NaOH. The emission intensity begins to increase almost immediately following the addition of NaOH. Prior to ferrocene oxidation or the addition of NaOH, the emission intensity of Rhodamine B was constant overnight, indicating that the dye remains trapped in the pores of the silica particles. In contrast to the CB7 system, deprotonation of the terminal carboxylic group by adding NaOH to a solution containing the dye-loaded β-CD-capped nanoparticles has a minimal effect on the host–guest interaction between β-CD and the ferrocenecarboxylate unit, leading to a smaller increase in the intensity of the emission of the Rhodamine B.

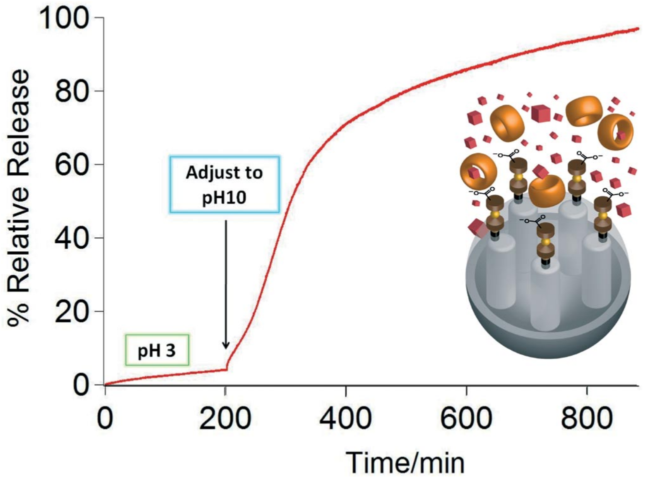

Figure 4. Release profile of Rhodamine B (RhB) from inside the nanopores of cucurbit[7]uril-capped MNPs. The emission of RhB in a pH = 3 aqueous TFA solution was monitored for 200 min prior to adjusting to pH = 10 by adding 1 N NaOH solution. After the addition, the emission intensities increase rapidly and then asymptotically approach their maximum with a time-to-half maximum release of around 100 min.

Conclusions

A new class of mechanized nanoparticles has been prepared and characterized. These mechanized nanoparticles operate under redox or pH control, depending on the nature of the ring capping the nanopores (β-CD in the first case and CB7 in the latter). These observations merely serve to underline just how broadly in terms of structure and mechanism the concept of mechanized nanoparticles, based on mesoporous silica, can be explored and exploited with equanimity in aqueous solutions, as well as in organic solvents.

Supporting Information (see footnote on the first page of this article): Synthesis, assembly, and characterization data of the β-CD- and CB7-capped ferrocene nanoparticles.

Acknowledgments

This work was supported by the Microelectronics Advanced Research Corporation (MARCO) and its focus center on Functional Engineered NanoArchitectonics (FENA), and by the Defense Threat Reduction Agency HDTRA1-08-1-0041 (J. F. S. and J. I. Z.) and NSF grant 0809384 (J. I. Z.).

---

[1] a) M. Vallet-Regi, A. Rámila, R. P. del Real, J. Pérez-Pariente, *Chem. Mater.* **2001**, *13*, 308–311; b) C. Barbé, J. Bartlett, L. Kong, K. Finnie, H. Q. Lin, M. Larkin, S. Calleja, A. Bush, G. Calleja, *Adv. Mater.* **2004**, *16*, 1959–1966; c) Q. Yang, S. Wang, P. Fan, L. Wang, Y. Di, K. Lin, F.-S. Xiao, *Chem. Mater.* **2005**, *17*, 5999–6003; d) F. Balas, M. Manzano, P. Horcajada, M. Vallet-Regí, *J. Am. Chem. Soc.* **2006**, *128*, 8116–8117; e) M. Arruebo, M. Galán, N. Navascués, C. Téllez, C. Marquina, M. R. Ibarra, J. Santamaría, *Chem. Mater.* **2006**, *18*, 1911–1919; f) S. Angelos, E. Choi, F. Vögtle, L. De Cola, J. I. Zink, *J. Phys. Chem. C* **2007**, *111*, 6589–6592; g) I. I. Slowing, B. G. Trewyn, V. S.-Y. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 8845–8849.

[2] T. D. Nguyen, K. C.-F. Leung, M. Liong, C. D. Pentecost, J. F. Stoddart, J. I. Zink, *Org. Lett.* **2006**, *8*, 3363–3366.

[3] K. C.-F. Leung, T. D. Nguyen, J. F. Stoddart, J. I. Zink, *Chem. Mater.* **2006**, *18*, 5919–5928.

[4] a) N. K. Mal, M. Fujiwara, Y. Tanaka, *Nature* **2003**, *421*, 350–353; b) N. Liu, D. R. Dunphy, P. Atanassov, S. D. Bunge, Z. Chen, G. P. Lopez, T. J. Boyle, C. J. Brinker, *Nano Lett.* **2004**, *4*, 551–554; c) T. D. Nguyen, K. C.-F. Leung, M. Liong, Y. Liu, J. F. Stoddart, J. I. Zink, *Adv. Funct. Mater.* **2007**, *17*, 2101–2110.

[5] a) R. Hernandez, H.-R. Tseng, J. W. Wong, J. F. Stoddart, J. I. Zink, *J. Am. Chem. Soc.* **2004**, *126*, 3370–3371; b) T. D. Nguyen, H.-R. Tseng, P. C. Celestre, A. H. Flood, Y. Liu, J. F. Stoddart, J. I. Zink, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10029–10034; c) T. D. Nguyen, Y. Liu, S. Saha, K. C.-F. Leung, J. F. Stoddart, J. I. Zink, *J. Am. Chem. Soc.* **2007**, *129*, 626–634.

[6] For recent reviews on nanovalves, see: a) S. Saha, K. C.-F. Leung, T. D. Nguyen, J. F. Stoddart, J. I. Zink, *Adv. Funct. Mater.* **2007**, *17*, 685–693; b) S. Angelos, E. Johansson, J. F. Stoddart, J. I. Zink, *Adv. Funct. Mater.* **2007**, *17*, 2261–2271.

[7] a) K. C.-F. Leung, T. D. Nguyen, J. F. Stoddart, J. I. Zink, *Chem. Mater.* **2006**, *18*, 5919–5928; b) S. Angelos, Y.-W. Yang, K. Patel, J. F. Stoddart, J. I. Zink, *Angew. Chem. Int. Ed.* **2008**, *47*, 2222–2226.

[8] J. C. Medina, T. T. Goodnow, M. T. Rojas, J. L. Atwood, B. C. Lynn, A. E. Kaifer, G. W. Gokel, *J. Am. Chem. Soc.* **1992**, *114*, 10583–10595.

[9] R. C. J. Atkinson, V. C. Gibson, N. J. Long, *Chem. Soc. Rev.* **2004**, *33*, 313–328.

[10] I. R. Whittall, A. M. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **1998**, *42*, 291–362.

[11] D. Astruc, *Electron Transfer and Radical Processes in Transition-Metal Chemistry*, VCH, New York, **1995**.

[12] D. R. van Staveren, N. Metzler-Nolte, *Chem. Rev.* **2004**, *104*, 5931–5985.

[13] S. Ferry-Forgues, B. Delavaux-Nicot, *J. Photochem. Photobiol. A: Chem.* **2000**, *132*, 137–159.

[14] a) I. Manners, *Adv. Organomet. Chem.* **1995**, *37*, 131–168; b) R. Castro, I. Cuadrado, B. Alonso, C. M. Casado, M. Morán, A. E. Kaifer, *J. Am. Chem. Soc.* **1997**, *119*, 5760–5761; c) C. M. Cardona, A. E. Kaifer, *J. Am. Chem. Soc.* **1998**, *120*, 4023–4024; d) R. D. A. Hudson, *J. Organomet. Chem.* **2001**, *637–639*, 47–69; e) A. S. Abd-El-Aziz, *Macromol. Rapid Commun.* **2002**, *23*, 995–1031; f) D. Sobransingh, A. E. Kaifer, *Chem. Commun.* **2005**, 5071–5073; g) D. Podkoscielny, I. Philip, C. L. D. Gibb, B. C. Gibb, A. E. Kaifer, *Chem. Eur. J.* **2008**, *14*, 4704–4710.

[15] a) S. Top, B. Dauer, J. Vaissermann, G. Jaouen, *J. Organomet. Chem.* **1997**, *541*, 355–361; b) S. Top, A. Vessières, G. Leclercq, J. Quivy, J. Tang, J. Vaissermann, M. Huché, G. Jaouen, *Chem. Eur. J.* **2003**, *9*, 5223–5236; c) Buriez, J. M. Heldt, E. Labbé, A. Vessières, G. Jaouen, C. Amatore, *Chem. Eur. J.* **2008**, *14*, 8195–8203; d) Z. Petrovski, M. R. P. Norton de Matos, S. S. Braga, C. C. L. Pereira, M. L. Matos, I. S. Gonçalves, M. Pillinger, P. M. Alves, C. C. Romão, *J. Organomet. Chem.* **2008**, *693*, 675–684.

[16] a) T. Matsue, D. H. Evans, T. Osa, N. Kobayashi, *J. Am. Chem. Soc.* **1985**, *107*, 3411–3417; b) A. Diaz, P. A. Quintela, J. M. Schuette, A. E. Kaifer, *J. Phys. Chem.* **1988**, *92*, 3537–3542; c) R. Isnin, C. Salam, A. E. Kaifer, *J. Org. Chem.* **1991**, *56*, 35–41; d) R. Isnin, A. E. Kaifer, *J. Am. Chem. Soc.* **1991**, *113*, 8188–8190; e) M. T. Rojas, R. Königer, J. F. Stoddart, A. E. Kaifer, *J. Am. Chem. Soc.* **1995**, *117*, 336–343; f) L. A. Godínez, S. Patel, C. M. Criss, A. E. Kaifer, *J. Phys. Chem.* **1995**, *99*, 17449–17455; g) L. A. Godínez, J. Lin, M. Muñoz, A. W. Coleman, A. E. Kaifer, *Electroanalysis* **1996**, *8*, 1072–1074; h) L. A. Godínez, L. Schwartz, C. M. Criss, A. E. Kaifer, *J. Phys. Chem. B* **1997**, *101*, 3376–3380; A. Mirzoian, A. E. Kaifer, *Chem. Eur. J.* **1997**, *3*, 1052–1058; i) S. A. Nepogodiev, J. F. Stoddart, *Chem. Rev.* **1998**, *98*, 1959–1976; j) Y. Wang, J. Alvarez, A. E. Kaifer, *Chem. Commun.* **1998**, 1457–1458; k) A. E. Kaifer, *Acc. Chem. Res.* **1999**, *32*, 62–71; l) Y. Wang, A. E. Kaifer, *J. Phys. Chem. B* **1998**, *102*, 9922–9927; m) J. Liu, S. Mendoza, E. Román, M. J. Lynn, R. Xu, A. E. Kaifer, *J. Am. Chem. Soc.* **1999**, *121*, 4304–4305; n) C. M. Cardona, T. D. McCarley, A. E. Kaifer, *J. Org. Chem.* **2000**, *65*, 1857–1864; o) J. Liu, W. Ong, E. Román, M. J. Lynn, A. E. Kaifer, *Langmuir* **2000**, *16*, 3000–3002; p) J. Liu, R. Castro, K. A. Abboud, A. E. Kaifer, *J. Org. Chem.* **2000**, *65*, 6973–6977; q) A. Harada, *Acc. Chem. Res.* **2001**, *34*, 456–464; r) J. Liu, J. Alvarez, W. Ong, E. Román, A. E. Kaifer, *Langmuir* **2001**, *17*, 6762–6764; B. González, I. Cuadrado, B. Alonso, C. M. Casado, M. Morán, A. E. Kaifer, *Organometallics* **2002**, *21*, 3544–3551.

[17] a) B. Siegel, R. Breslow, *J. Am. Chem. Soc.* **1975**, *97*, 6869–6870; b) G. L. Trainor, R. Breslow, *J. Am. Chem. Soc.* **1981**, *103*, 154–158; c) R. Breslow, G. Trainor, A. Ueno, *J. Am. Chem. Soc.* **1983**, *105*, 2739–2744.

[18] a) R. C. Sabapathy, S. Bhattacharyya, W. E. Cleland Jr, C. L. Hussey, *Langmuir* **1998**, *14*, 3797–3807; b) J. Liu, R. Castro, K. A. Abboud, A. E. Kaifer, *J. Org. Chem.* **2000**, *65*, 6973–6977.

[19] a) A. Harada, S. Takahashi, *J. Chem. Soc., Chem. Commun.* **1984**, *10*, 645–646; b) B. González, I. Cuadrado, B. Alonso, C. M. Casado, M. Morán, A. E. Kaifer, *Organometallics* **2002**, *21*, 3544–3551.

[20] a) J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2000**, *122*, 540–541; b) A. Day, A. P. Arnold, R. J. Blanch, B. Snushall, *J. Org. Chem.* **2001**, *66*, 8094–8100; c) W. Ong, M. Gamez-Kaifer, A. E. Kaifer, *Org. Lett.* **2002**, *4*, 1791–1794; d) K. Moon, A. E. Kaifer, *Org. Lett.* **2004**, *6*, 185–188; e) S. Liu, P. Y. Zavalij, L. Isaacs, *J. Am. Chem. Soc.* **2005**, *127*, 16798–16799; f) T. Ooya, D. Inoue, H. S. Choi, Y. Kobayashi, S. Loethen, D. H. Thompson, Y. H. Ko, K. Kim, N. Yui, *Org. Lett.* **2006**, *8*, 3159–3162; g) A. M. Rawashdeh, A. Thangavel, C. Sotiriou-Leventis, N. Leventis, *Org. Lett.* **2008**, *10*, 1131–1134.

[21] W. Ong, A. E. Kaifer, *Organometallics* **2003**, *22*, 4181–4183.

[22] W. S. Jeon, K. Moon, S. H. Park, H. Chun, Y. H. Ko, J. Y. Lee, E. S. Lee, S. Samal, N. Selvapalam, M. V. Rekharsky, V. Sindelar, D. Sobransingh, Y. Inoue, A. E. Kaifer, K. Kim, *J. Am. Chem. Soc.* **2005**, *127*, 12984–12989.

[23] J. Liu, S. Mendoza, E. Román, M. J. Lynn, R. Xu, A. E. Kaifer, *J. Am. Chem. Soc.* **1999**, *121*, 4304–4305.

[24] To ensure the maximum of contact of the nanoparticles with the Pt grid, the solution was stirred slowly. The presence of the nanoparticles as a suspension in solution affects the base line and raises it as shown in Figure 3.

Received: December 30, 2008