

Interfacially Cross-Linked Reverse Micelles as Soluble Support for Palladium Nanoparticle Catalysts

by Li-Chen Lee and Yan Zhao*

Department of Chemistry, Iowa State University, Ames, IA 50011-3111, USA
(phone: +1-515-2945845; fax: +1-515-2940105; e-mail: zhaoy@iastate.edu)

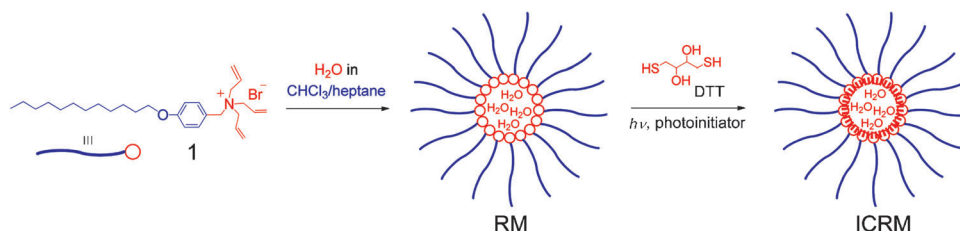
Reverse micelles (RM) were formed in heptane/ CHCl_3 with a surfactant carrying the triallylammonium (= triprop-2-en-1-ylammonium) head group (*Scheme*). Photo-cross-linking with dithiothreitol (= *rel*-(2*R*,3*R*)-1,4-dimercaptobutane-2,3-diol; DTT) captured the RMs and afforded organic, soluble nanoparticles in a one-step reaction. Similar to dendrimers, the cross-linked reverse micelles could encapsulate palladium nanoparticles within their hydrophilic cores and protect them in catalytic reactions. Good to excellent yields were obtained in the *Heck* coupling of a range of alkyl acrylates (= alkyl prop-2-enoates) and iodobenzenes (*Tables 1* and *2*). The catalytic activity of the palladium nanoparticles was maintained in several repeated runs.

Introduction. – By staying in the same phase and being readily accessible to reactants, homogeneous catalysts may achieve very high activity. Their mechanistic understanding and optimization in activity/selectivity are facilitated by the systematic tuning of the ligand environments and active sites. Heterogeneous catalysts, on the other hand, often distinguish themselves by the ease of product separation, long-term stability, and recyclability. Chemists have long sought to bridge the gap between the two catalyst types and create either heterogenized homogeneous catalysts or soluble versions of heterogeneous catalysts [1]. Metal nanoparticles find many applications in both homogeneous and heterogeneous catalysis because their large surface area translates to a high percentage of surface atoms useful for catalysis [1–4]. When deposited on solid supports, however, metal nanoparticles tend to vary greatly in size, shape, and aggregational state, making it challenging to control the active sites and selectivity in the reactions [5]. For these and other reasons, there have been intensive efforts to identify suitable organic supports to stabilize metal nanoparticles, in the hope that the organic supports may not only create more uniform metal nanoparticles but also provide additional features not available to their inorganic counterparts [1–4]. Organic dendrimers [6], for example, have been shown to offer a range of useful features including size selectivity [7], tailored solubility [8][9], and improved surface deposition [5].

We recently reported a simple method to capture reverse micelles covalently [10]. Reverse micelles (RMs) are widely used as templates to create inorganic nanoparticles, but the dimension of the final materials templated by RMs rarely correlates directly with the size of the templates [11][12]. The discrepancy derives from fast collision of RMs, accompanied by coalescence and rapid exchange of the internal contents [13][14]. Although covalent fixation of RMs should in principle solve these problems,

the same problems in the RM-templated synthesis (*i.e.*, fast collision and coalescence) make it difficult to capture the dynamic noncovalent assemblies in the original states [15][16]. Our covalent capture of RM relies on the three allyl (= prop-2-en-1-yl) groups in the headgroup of 4-(dodecyloxy)-*N,N,N*-triprop-2-en-1-ylbenzenemethanaminium bromide (**1**), which create a high density of alkene functionality at the surfactant–H₂O interface (*Scheme*). When a H₂O-soluble cross-linker, dithiothreitol (*rel*-(2*R*,3*R*)-1,4-dimercaptobutane-2,3-diol; DTT), is used, the efficient thiol–ene radical addition [17–19] is facilitated by the proximity and high local concentration of the thiol and the alkene moieties. The high cross-linking density near the head group is also important to the successful capture of the RMs in the original size [20][21].

Scheme. Preparation of Interfacially Cross-Linked Reverse Micelles (ICRMs) by the Thiol–Ene Addition



In this work, we report our first step in using interfacially cross-linked RMs (ICRMs) as soluble support for Pd nanoparticles and demonstrate their applications in the *Heck* coupling. The *Heck* reaction belongs to an extremely important class of C,C bond-formation reactions [22][23]. Although phosphine ligands are well-known to stabilize the catalytically active Pd⁰ species for *Heck* reactions, they could be quite expensive. Similar to most homogeneous catalysts, recovery and reuse of catalysts are often impossible [24]. In addition to various inorganic supports [24][25], organic polymers [26][27], dendrimers [28–31], lyotropic liquid crystal polymers [32], block copolymer micelles [33][34], and polyhedral oligomeric silsesquioxane [35] have been reported to afford catalytically active Pd nanoparticles for the *Heck* coupling. With Pd-ICRM composites, we were able to perform efficient *Heck* reactions between iodoarenes and various acrylates (= prop-2-enoates). No palladium black was observed even after several reaction cycles. An important benefit of the ICRMs is their good miscibility with common organic reactants, allowing us to perform the *Heck* reaction without any solvents.

Results and Discussion. – ICRMs are unique templates for metal nanoparticles. Our previous work shows that single or bimetallic nanoparticles could be prepared simply by extraction of anionic metal salts such as AuCl₄[–] and PtCl₆^{2–} followed by reduction [10]. Because the interior of the ICRMs mainly contains weak ligands such as bromide, thioether, and OH groups, we reasoned that they should serve as useful support for catalytic nanoparticles. Our hypothesis was that the metal particle inside an ICRM would be stabilized mainly by physical protection and thus remains catalytically active. The rationale for the work was that the ICRMs resemble dendrimers in the multivalent

surface functionality and a well-defined core–shell structure but are prepared in a one-step synthesis. If they can duplicate the key benefits of dendrimer templates [6], the ease of synthesis would make them attractive for large-scale applications.

The details of ICRM synthesis were reported previously [10]. Briefly, optically clear RM solutions were prepared in heptane/ CHCl_3 2:1 with $[\text{H}_2\text{O}]/[\mathbf{1}] = 5$. CHCl_3 was included mainly to help dissolve DTT, the cross-linker, in the nonpolar mixture. Upon photolysis in the presence of 0.5 mol-% of the photoinitiator 2,2'-dimethoxy-2-phenylacetophenone (=2-methoxy-1-(2-methoxyphenyl)-1-phenylethanone), an efficient thiol–ene radical reaction [17–19] took place. As reported previously, the ICRMs were characterized by a range of techniques including ^1H -NMR spectroscopy, dynamic light scattering (DLS), transmission electron microscopy (TEM), and IR spectroscopy [10]. The ICRMs can interact with one another through *van der Waals* interactions of the alkyl chains on the surface. Their cores consist of charged ammonium head groups, and aggregation thus can benefit as well from electrostatic interactions, which could operate over a long distance. A double-tailed surfactant afforded ICRMs free of aggregation. We chose to use the single-tailed surfactant because the lower density of alkyl coronas was possibly beneficial to mass transfer. Although the ICRMs of the single-tailed surfactant **1** aggregated in a solvent-dependent fashion, the aggregates (13 nm in diameter in THF and *ca.* 200 nm in CHCl_3) were completely soluble in solvents with intermediate polarity but insoluble in highly polar (*e.g.*, MeOH or H_2O) or highly nonpolar solvents such as hexane.

Because an ICRM contains numerous ammonium head groups in the interior, it is most suited to extract anionic metal precursors. When a solution of H_2PdCl_4 (10 mM) in H_2O (2 ml) was stirred with a solution of ICRM ($[\mathbf{1}] = 10$ mM) in CHCl_3 (2 ml), the orange phase turned colorless, and the organic layer became orange, indicating the successful extraction of the metal salts into the ICRMs.

Many reducing agents including sodium borohydride [28][31][34], superhydride [33], and EtOH [26] were reported to convert Pd^{II} to Pd^0 . When the above described Pd-containing ICRM solution was heated to reflux in the presence of EtOH (2 ml) for 3 h, a brownish orange solution was obtained. No palladium black or precipitate was formed during the process, indicating that the reduced palladium was protected by the ICRMs. After evaporation of the solvents, the materials obtained could be redissolved in common organic solvents such as CHCl_3 , CH_2Cl_2 , and THF. The solution was stable over at least a period of several months.

In our catalytic study (*vide infra*), we attempted *Heck* reactions with the Pd-ICRMs without EtOH treatment because Et_3N , the base used in our *Heck* coupling, is known to reduce Pd^{II} during the reaction [24]. Since the materials with and without EtOH reduction essentially afforded the same yields (*vide infra*), we adopted the simpler preparative procedure without the reduction step.

The UV/VIS spectra of the ICRMs and the Pd-ICRMs with and without EtOH treatment are shown in *Fig. 1*. The ICRMs had a major peak at 280 nm from the aromatic groups of the ICRMs (see structure of **1**). The major absorption of aqueous H_2PdCl_4 solution had a weak broad absorption at 420 nm. After loading with the palladium salt, the Pd-ICRMs had a very broad absorption band that started from 300 nm and tailed off into the VIS region. Overall, the materials obtained with and without EtOH reduction looked very similar. Possibly, some or all of the palladium salts

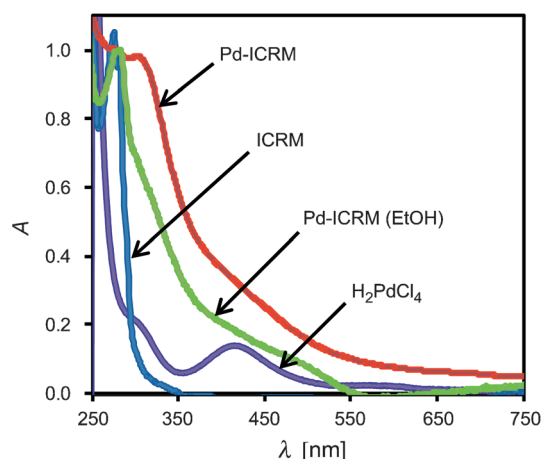


Fig. 1. UV/VIS Spectra of CHCl_3 solutions of ICRM, Pd-ICRM, and Pd-ICRM after EtOH treatment. $[\mathbf{1}] = 0.1 \text{ mM}$; $[\text{H}_2\text{PdCl}_4] = 0.1 \text{ mM}$. The spectra were adjusted in intensity for easier comparison.

were already reduced after extraction into the ICRMs. According to our previous study, AuCl_4^- extracted into the cores of the ICRMs could reduce spontaneously [10].

We also characterized the Pd-ICRM without EtOH treatment by TEM. Fig. 2 shows the representative micrograph of an unstained Pd-ICRM sample. The Pd nanoparticles showed up as dark spots and averaged *ca.* 2 nm in diameter, in line with the core size of the ICRMs. The ICRMs also seemed to cluster together, possibly due to the aggregation of the alkyl shell.

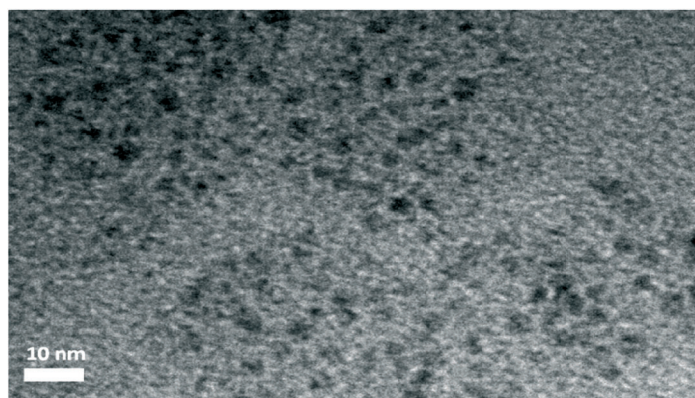


Fig. 2. Micrograph of Pd-ICRM without EtOH treatment, obtained by TEM

Initially, we were not sure whether the Pd-ICRMs would be catalytically active and stable during reactions. Soluble palladium clusters are known to form from Pd-nanoparticles and are responsible for catalyzing cross-coupling reactions [36][37]. Without ligands, Pd^0 is quite unstable and tends to quickly form palladium black and lose activity [22–24]. Therefore, after Pd-atoms depart from the ICRM cores and move

into the solution, even if these atoms are initially active, they would aggregate easily and precipitate. To our delight, when a 1 : 2 mixture of iodobenzene and butyl acrylate (= butyl prop-2-enoate) were heated with 1 mol-% of Pd-ICRMs and 1.2 equiv. of Et₃N at 80°, reaction ran cleanly (*Fig. 3*). After 18 h, the limiting reagent, iodobenzene, disappeared completely, and cinnamate was obtained as the only product. No solvent was needed in the reaction, suggesting that the Pd-ICRMs were completely miscible with the reactants, and the Pd metal inside the cores was readily accessible to the reactants. Importantly, the reaction mixture stayed completely clear at the end of the reaction, showing no formation of palladium black.

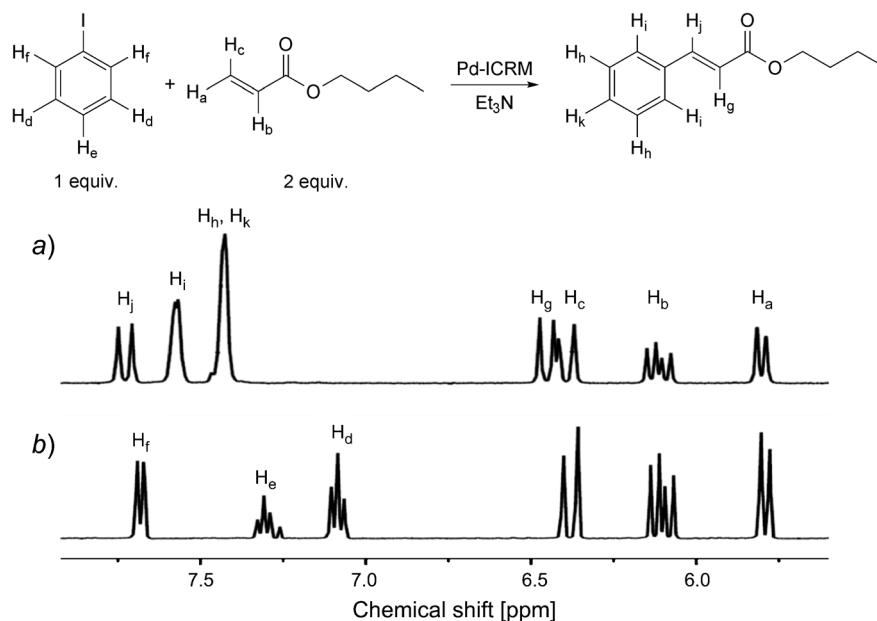


Fig. 3. ¹H-NMR Spectra of a) the reaction mixture and b) a 1 : 2 mixture of iodobenzene and butyl acrylate

Table 1 shows the yields of the Heck reaction between various alkyl acrylates and iodobenzene catalyzed by the Pd-ICRMs. As mentioned earlier, EtOH reduction made no difference in the catalysis (*Entries 1* and *2*), possibly because either Pd^{II} was already reduced during the Pd-ICRM preparation or reduced by the Et₃N added [24]. *t*-Butyl acrylate and the hydrophilic 2-hydroxyethyl acrylate both gave good yields, suggesting that both hydrophobic and hydrophilic substrates are able to penetrate the core of the cross-linked reverse micelles. The 2-ethylhexyl acrylate was less reactive, giving a modest yield of 68% (*Entry 5*). Initially, we thought the lower yield was caused by the alkyl corona of the ICRM having ‘filtering’ effects, similar to those found in high-generation dendrimers [7]. To probe the reason for lower yield, we allowed a 1 : 1 mixture of butyl acrylate and 2-ethylhexyl acrylate to react with 1 equivalent of iodobenzene and found that both acrylates were converted by similar rates. The lower conversion in 2-ethylhexyl acrylate, therefore, could not come from the filtering effect mentioned above. We also performed some control experiments. Without protection by

Table 1. Pd-ICRM-Catalyzed Heck Reactions Between Alkyl Acrylate and Iodobenzene

Entry	R	Yield [%] ^{a)}
1	Bu	> 95
2	Bu	> 95 ^{b)}
3	<i>t</i> -Bu	94
4	2-hydroxyethyl	93
5	2-ethylhexyl	68
6	Bu	> 95 ^{c)}
7	Bu	0 ^{d)}

^{a)} Yields of the products were determined by ¹H-NMR analysis. A yield of >95% means that the reaction went to completion with no detectable amount of iodobenzene by ¹H-NMR spectroscopy. Typical reaction conditions: alkyl acrylate (1.0 mmol), iodobenzene (0.5 mmol), Et₃N (0.6 mmol), and Pd-ICRM (1 mol-% of Pd with respect to iodobenzene); at 80° for 18 h. In *Entry 4*, 1 equiv. of acrylate was used. ^{b)} Pd-ICRM with EtOH reduction was used. ^{c)} H₂PdCl₄ was used. Although the reaction proceeded well, a large amount of palladium black formed during the coupling. ^{d)} ICRMs in the absence of Pd were used.

the ICRMs, H₂PdCl₄ was insoluble in the reaction mixture and gave palladium black immediately. Although complete conversion of the butyl acrylate was also observed, the reaction, after 18 h, produced a large amount of black precipitate (*Entry 6*). In the absence of Pd, the ICRMs, as expected, were unable to promote the reaction (*Entry 7*).

The catalysis could happen in two possible ways. First, Pd⁰-atoms departed from the stock of palladium in the ICRM cores and moved into the solution to catalyze the reaction. Second, the reactions mostly took place on the surface of the Pd nanoparticles, and catalytically active species never moved too far away from the ICRM cores. Our data could not rule out either mechanism. Because H₂PdCl₄ without the ICRMs also catalyzed the *Heck* coupling (*Table 1, Entry 6*), the ICRMs were not necessary for the reaction to occur. On the other hand, since H₂PdCl₄ without the ICRMs produced a large amount of palladium black, the ICRMs were clearly helpful by stabilizing Pd⁰. Most likely, even if Pd⁰ migrated from the ICRM cores and went into the solution to catalyze the reaction, the amount of Pd⁰ departed must be so small that visible palladium, *i.e.*, large aggregates of Pd⁰ could not form. Alternatively, because the high tendency for Pd⁰ to agglomerate, the Pd⁰ atoms or small clusters that went into the solution may return and merge with the Pd nanoparticles within the ICRM cores. It should be noted that palladium black was never observed in Pd-ICRM-catalyzed reactions even in repeated runs (*vide infra*).

The results so far are quite promising. Despite the simpler synthesis and structure, the Pd-ICRMs gave comparable results as dendrimer-protected Pd nanoparticles in *Heck* coupling [28–31]. The good miscibility of the ICRMs with organic reactants is noteworthy, as solventless conditions are attractive for both economical and environmental points of view. To study the scope of the reaction, we examined the coupling

between butyl acrylate and a range of substituted iodobenzenes, with electron-donating and -withdrawing groups at different positions. Most reactions proceeded well and gave good to excellent yields. On average, electron-deficient iodobenzenes gave somewhat higher yields than the electron-rich ones (*Table 2*).

Table 2. *Pd-ICRM-Catalyzed Heck Reactions between Butyl Acrylate and Substituted Iodobenzenes*

R'	Yield [%] ^{a)}
H	> 95
2-Me	82
2-MeO	78
2-Br	95
3-Br	> 95
3-NO ₂	> 95
2-NO ₂ and 5-MeO	88
4-Br	89
4-NO ₂	78
4-CN	82
4-MeO	84

^{a)} Yields of the products were determined by ¹H-NMR analysis. A yield of >95% means that the reaction went to completion with no detectable amount of iodobenzene by ¹H-NMR spectroscopy. Typical reaction conditions: alkyl acrylate (1.0 mmol), iodobenzene (0.5 mmol), Et₃N (0.6 mmol), and Pd-ICRM (1 mol-% of Pd with respect to iodobenzenes; at 80° for 18 h).

To test the reusability of the Pd-ICRMs, we took a mixture of butyl acrylate, iodobenzene, Et₃N, and 1 mol-% Pd-ICRMs and heated it to 80°. After 18 h, another batch of reactants without the extra equivalent of butyl acrylate was added. ¹H-NMR spectroscopy indicated complete conversion of the iodobenzene. The procedure was repeated and, after the third cycle, the yield still remained quite good (85%). It is worth mentioning that the reaction mixture stayed clear throughout the three cycles and showed no formation of palladium black at the end of the third reaction cycle (*Fig. 4*). The lower yield in the third cycle could result from surface-poisoning of the nanoparticles. Similar results were reported in dendrimer-encapsulated Pd nanoparticles [28]. We also attempted to use the Pd-ICRMs for the *Heck* reactions of bromo- and chloroarenes but found them to be much less reactive. The results most likely derived from limitation of the Pd nanoparticles because similar observations were made in dendrimer-encapsulated Pd nanoparticles [28–31].

Conclusions. – In summary, ICRMs are an excellent soluble support for catalytically active Pd nanoparticles. Good to excellent yields were obtained for the *Heck* coupling of a wide range of alkyl acrylates and iodobenzenes. The catalytic cores were readily accessible to most reagents. Compared to dendrimer templates, the ICRMs are much easier to prepare, *via* a one-step photo-cross-linking reaction. Extraction of metal salts

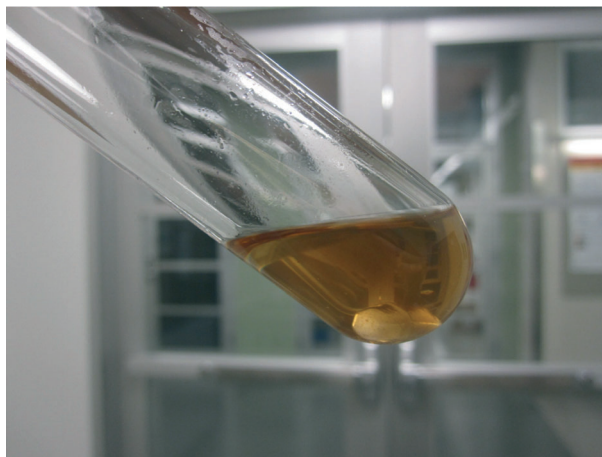


Fig. 4. Photograph of the reaction mixture of butyl acrylate and iodobenzene after the third catalytic cycle

is straightforward. Although the current systems only extract anionic salts, similar cross-linking concepts can be applied to anionic and nonionic surfactants, as long as they carry multiple C=C bonds near the head group. The ICRMs are insoluble in polar organic solvents (MeOH or EtOH) and, if needed, can be easily recovered by precipitation. We demonstrated some success in reusing the catalysts for multiple runs. Given the simplicity of the synthesis and easy modification of the surfactants, ICRMs with a wide range of properties should be readily available, making these materials potentially useful in many catalytic applications.

Experimental Part

General. All reagents and solvents were of A.C.S. certified grade or higher, and were used as received from commercial suppliers. The synthesis and characterization of ICRMs were reported previously [10]. UV/VIS Spectra: *Cary-50-Bio* UV/VIS spectrophotometer; at r.t.. TEM: *Philips-CM-30* instrument, operating at 200 kV. ¹H-NMR Spectra: *Varian-VXR-400* and *Bruker DRX-400* spectrometer; δ in ppm rel. to Me₄Si as internal standard, *J* in Hz.

Typical Preparation of Pd-ICRMs. An aq. soln. of H₂PdCl₄ (10 mM) was prepared by adding 0.4M HCl (6 ml) to PdCl₂ (1.2 mmol) in H₂O (114 ml). A portion (2 ml) of this H₂PdCl₄ soln. was added to an ICRM soln. in CHCl₃ (2 ml, [1] = 10 mM). After stirring overnight, the mixture was allowed to sit at r.t. The orange org. phase was separated, washed with H₂O (3 ×), and concentrated to give an orange powder. For the UV/VIS measurement, 0.1 ml of the CHCl₃ soln. was diluted by 9.9 ml of CHCl₃ so that the concentration of the cross-linked [1] was 0.1 mM in the final sample.

Typical Preparation of Pd-ICRMs with EtOH as the Reducing Agents. The Pd-ICRMs were prepared as above. The CHCl₃ layer was separated and combined with 2 ml of EtOH. The resulting mixture was heated to reflux under N₂ for 3 h. After the soln. was cooled to r.t., the org. layer was washed with H₂O and concentrated to give a brownish orange powder. For the UV/VIS measurement, 2 ml of CHCl₃ was added back to the above-described brownish orange powder. A portion (0.1 ml) of the CHCl₃ soln. was diluted by 9.9 ml of CHCl₃ so that the concentration of cross-linked 1 was 0.1 mM in the final sample.

TEM Imaging. A soln. of Pd-ICRM in THF ([1] = 1.0 · 10⁻⁴ M) was gently placed on a C-atom-coated copper grid (C-atom type A, 300 mesh). The TEM grid was dried overnight at r.t., and subjected to TEM observation.

Typical Procedure for the Heck Reaction. A small *J. Young* tube was charged with butyl acrylate (143.4 μ l, 1 mmol), iodobenzene (56 μ l, 0.5 mmol), Et₃N (83.6 μ l, 0.6 mmol), and the Pd-ICRM catalyst ([Pd] = [1] = 0.005 mmol). The mixture was stirred at 80° for 18 h with the tube closed. After the mixture was cooled to r.t., CDCl₃ was added, and yield of the reaction was determined by ¹H-NMR spectroscopy.

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REFERENCES

- [1] G. A. Somorjai, A. M. Contreras, M. Montano, R. M. Rioux, *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10577.
- [2] D. Astruc, in 'Nanoparticles and Catalysis', Ed. D. Astruc, Wiley-VCH, Weinheim, Germany, 2008.
- [3] A. T. Bell, *Science (Washington, DC, U.S.)* **2003**, *299*, 1688.
- [4] C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, *105*, 1025.
- [5] G. A. Somorjai, Y. M. Li, *Top. Catal.* **2010**, *53*, 832.
- [6] R. M. Crooks, M. Zhao, L. Sun, V. Chechik, L. K. Yeung, *Acc. Chem. Res.* **2001**, *34*, 181.
- [7] M. Zhao, R. M. Crooks, *Angew. Chem., Int. Ed.* **1999**, *38*, 364.
- [8] V. Chechik, M. Zhao, R. M. Crooks, *J. Am. Chem. Soc.* **1999**, *121*, 4910.
- [9] V. Chechik, R. M. Crooks, *J. Am. Chem. Soc.* **2000**, *122*, 1243.
- [10] S. Zhang, Y. Zhao, *ACS Nano* **2011**, *5*, 2637.
- [11] J. H. Fendler, 'Membrane Mimetic Chemistry', Wiley, New York, 1982.
- [12] M. P. Pileni, 'Structure and Reactivity in Reverse Micelles', Elsevier, Amsterdam, 1989.
- [13] M. P. Pileni, *Langmuir* **1997**, *13*, 3266.
- [14] M.-P. Pileni, *Nat. Mater.* **2003**, *2*, 145.
- [15] G. Voortmans, A. Verbeeck, C. Jackers, F. C. De Schryver, *Macromolecules* **1988**, *21*, 1977.
- [16] G. Voortmans, F. C. De Schryver, in 'Polymerization in and of Inverse Micelles', Ed. M. P. Pileni, Elsevier, Amsterdam, 1989.
- [17] A. Dondoni, *Angew. Chem., Int. Ed.* **2008**, *47*, 8995.
- [18] C. E. Hoyle, T. Y. Lee, T. Roper, *J. Polym. Sci. Pol. Chem.* **2004**, *42*, 5301.
- [19] R. K. Iha, K. L. Wooley, A. M. Nyström, D. J. Burke, M. J. Kade, C. J. Hawker, *Chem. Rev.* **2009**, *109*, 5620.
- [20] H. M. Jung, K. E. Price, D. T. McQuade, *J. Am. Chem. Soc.* **2003**, *125*, 5351.
- [21] K. E. Price, D. T. McQuade, *Chem. Commun.* **2005**, 1714.
- [22] R. F. Heck, *Acc. Chem. Res.* **1979**, *12*, 146.
- [23] R. F. Heck, 'Palladium Reagents in Organic Synthesis', Academic Press, London, 1985.
- [24] I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009.
- [25] A. Biffis, M. Zecca, M. Basato, *J. Mol. Catal. A: Chem.* **2001**, *173*, 249.
- [26] S. Pathak, M. T. Greci, R. C. Kwong, K. Mercado, G. K. S. Prakash, G. A. Olah, M. E. Thompson, *Chem. Mater.* **2000**, *12*, 1985.
- [27] K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida, S. Kobayashi, *J. Am. Chem. Soc.* **2005**, *127*, 2125.
- [28] L. K. Yeung, R. M. Crooks, *Nano Lett.* **2000**, *1*, 14.
- [29] E. H. Rahim, F. S. Kamounah, J. Frederiksen, J. B. Christensen, *Nano Lett.* **2001**, *1*, 499.
- [30] L. K. Yeung, C. T. Lee Jr., K. P. Johnston, R. M. Crooks, *Chem. Commun.* **2001**, 2290.
- [31] K. R. Gopidas, J. K. Whitesell, M. A. Fox, *Nano Lett.* **2003**, *3*, 1757.
- [32] J. H. Ding, D. L. Gin, *Chem. Mater.* **2000**, *12*, 22.
- [33] S. Klingelhöfer, W. Heitz, A. Greiner, S. Oestreich, S. Förster, M. Antonietti, *J. Am. Chem. Soc.* **1997**, *119*, 10116.
- [34] I. P. Beletskaya, A. N. Kashin, A. E. Litvinov, V. S. Tyurin, P. M. Valetsky, G. van Koten, *Organometallics* **2005**, *25*, 154.
- [35] C.-H. Lu, F.-C. Chang, *ACS Catal.* **2011**, *1*, 481.
- [36] M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, 1559.
- [37] D. Astruc, *Inorg. Chem.* **2007**, *46*, 1884.

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