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Preparation of Cadmium Selenide−Polyolefin Composites from Functional Phosphine Oxides and Ruthenium-Based Metathesis

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Abstract: Cadmium selenide nanoparticles, prepared by known methods, were stabilized with functional phosphine oxide **1**, then used to support the polymerization of cyclic olefins radially outward from the surface by ruthenium-catalyzed ring-opening metathesis polymerization (ROMP). The conversion of compound **1** into the new metathesis catalyst **3** by carbene exchange and the subsequent polymerization of cyclic olefins were observed spectroscopically by ^{1}H NMR to afford for example CdSe−polycyclooctene composite **6**. Transmission electron micrographs on thin films of these composites showed good nanoparticle dispersion. This is in stark contrast to the substantial nanoparticle aggregation observed when similar polymerizations were performed in the presence of conventional TOPO-covered nanoparticles. The methods reported here to prepare composite product **6** are applicable to other cyclic olefins, and suggest that this chemistry will be useful for incorporating CdSe nanoparticles into a wide variety of polymer matrices.

Introduction

Current research in nanoscopic science[1,2] ranges from fundamental synthesis and self-assembly to applied electronic and biological targets. Within various nanotechnologies are critical challenges associated with the ability to produce controlled and ordered nanoscale structures that achieve or approach desired applications. Semiconductor nanoparticles, or “quantum dots”, are promising candidates for use as active components in materials for both nanoelectronics[3] and biotechnology.[4] Such materials are characterized by their well-defined dimensions (2−8 nm diameter ±5−10%) and unique properties, intermediate between molecular and bulk material. Properties such as narrow luminescence profiles over a broad excitation range are critical for nanoparticle-based devices including biological probes, LED displays, tunable lasers, and photovoltaic cells. For many applications, nanoparticles must be dispersible in a variety of matrices, where aggregation and agglomeration phenomena are suppressed. However, the high surface energy and inherent instability (e.g. tendency toward oxidation) of many nanoparticles present substantial challenges in this regard.

CdSe nanoparticles have typically been prepared from Cd$(CH_3)_2$ and Se(0) by high-temperature (300−350 °C) nucleation and growth conditions in phosphorus-based surfactant ligands.[5] Recent studies by Peng and co-workers[6] have increased the accessibility of CdSe nanoparticles by employing more easily handled cadmium sources, such as CdO. Both methods give well-defined nanoparticles containing a periphery of encapsulating aliphatic phosphines, phosphine oxides, and/or phosphonic acids bound to surface cadmium. While this organic periphery provides surface passivation, its aliphatic nature affords hydrophobic materials with an inert peripheral shell. On the other hand, organic thiols containing chain-end functionality have also been employed to encapsulate CdSe, where surface binding through the thiol leaves hydrophilic moieties exposed to the environment; these can be used to promote water solubility and/or for performing further chemistry.[7,8] However, the use of thiol

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(6) (a) Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *123*, 183. (b) typical CdSe nanoparticle samples for work presented herein ranged from 3 to 3.4 nm diameter, with a λ_{max} absorbance ∼530 nm, and photoluminescence emission ∼560 nm.

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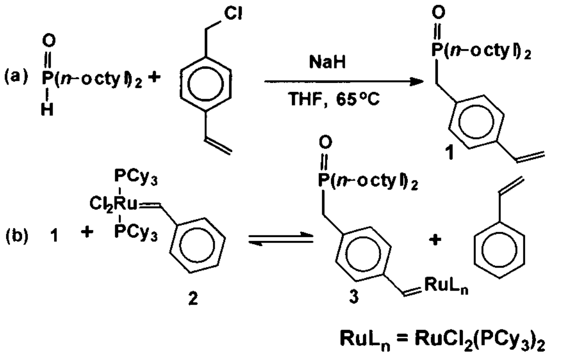
Scheme 1



encapsulants can lead to disulfide formation, which results in loss of surface coverage and thus oxidation/degradation processes on the nanoscopic structure.

Herein we describe our use of functional phosphine oxides for CdSe nanoparticle encapsulation and surface-initiated chain growth, where we target composites that retain the nanostructural integrity of the starting material and that display good particle dispersion. Such dispersion is typically difficult to achieve when such structurally disparate components are employed. Furthermore, the aliphatic periphery of the commonly prepared tri-*n*-octylphosphine oxide (TOPO)-covered nanoparticles precludes their dispersed incorporation into many polymers and hydrophilic solvents. Bawendi[3b] and Schrock and Thomas[9] have shown that CdSe nanoparticle aggregation can be avoided by judicious choice of monomers used for the composite material. While these reports represent excellent advances in CdSe–polymer hybrids, they are limited in scope in that they require either the use of monomers containing long aliphatic chains to promote miscibility with TOPO-covered nanoparticles (where the ligand environment around the nanoparticle remains unchanged)[3b] or multistep syntheses of ligand-containing monomers that then afford multiple polymer–nanoparticle interactions in the product.[9] In our approach we endeavor to expand the chemical accessibility and versatility of such composites by modifying the surface-bound ligands on CdSe in order to mimic TOPO coverage and simultaneously provide surface functionality for polymerization. For this we prepared ligand **1**, *p*-vinylbenzyl-DOPO (DOPO = di-*n*-octylphosphine oxide), for attachment to the CdSe surface and subsequent initiation of ring-opening metathesis polymerization (ROMP). While Mirkin and Nguyen demonstrated ROMP from gold nanoparticles using norbornene functionalized thiols,[10] our studies combine (1) the use of new phosphine oxide ligands that we believe are in many cases better suited for CdSe than thiols and (2) polymerization chemistry on CdSe nanoparticles, which have very attractive luminescent properties, and surface/periphery chemistry that is much less explored relative to gold nanoparticles.

Results and Discussion

Ligand **1** was synthesized by the reaction of DOPO (prepared separately[11]) with 4-vinylbenzyl chloride under basic conditions (Scheme 1a), and purified by crystallization from hexanes. Its ^{1}H NMR spectrum confirms the phosphine oxide-to-benzyl attachment (benzyl CH_2 resonance at δ 3.1 ppm), and the ^{31}P spectrum consists of one resonance at δ 47.3 ppm, typical of a trialkyl phosphine oxide. As compound **1** would be unstable at the high temperatures required for CdSe growth, **1**-covered nanocrystals were prepared by ligand exchange chemistry. TOPO-covered CdSe nanoparticles of approximately spherical shape were prepared,[6] and TOPO was removed from the surface (to give poorly soluble particles) and replaced with compound **1** by ligand exchange in dry THF. Surface coverage by the newly introduced phosphine oxide was implied by renewed particle solubility that gave optically transparent, colored solutions, and verified by ^{1}H and ^{31}P NMR spectroscopy, where resonances of **1** were observed, and those of TOPO were not. The interparticle separation evident by transmission electron microscopy (TEM) images further confirmed successful surface coverage (Figure 1). Confirmation that compound **1** is capable of nanoparticle passivation in a manner that resembles TOPO coverage was critical for proceeding with our polymerization studies.

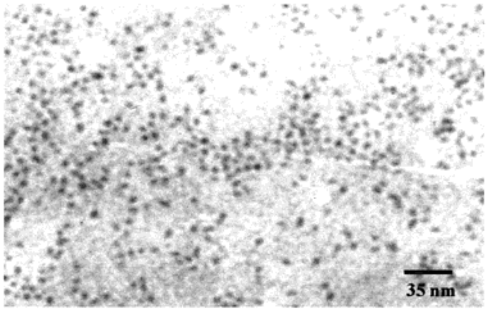


Figure 1. TEM micrograph of **1**-covered CdSe nanoparticles.

Control experiments were then performed in the absence of nanoparticles, first by addition of **1** to a solution of bis(tricyclohexylphosphine) benzylideneruthenium dichloride (**2**) in CH_2Cl_2 (Scheme 1b).[12] This gave an equilibrium mixture of **2** and a new ruthenium benzylidene catalyst **3** containing the DOPO-vinylbenzyl moiety, as evidenced by ^{1}H NMR spectroscopy (benzylidene resonances at δ 19.97 and 19.91 ppm for unreacted **2** and exchange product **3**, respectively). The relative amounts of **2** and **3** can be controlled based on the added amount of catalyst **2**, such that **2** is consumed completely if desired (see Supporting Information for details). In addition, new resonances at δ 3.0 ppm are assigned to the benzyl CH_2–P protons of **3**. We then demonstrated that compound **3** can be used successfully in ring-opening metathesis polymerization, as noted by the disappearance of both benzylidene signals upon addition of cyclic olefins to this equilibrium mixture. These polymerizations were performed at room temperature to give, for example in the case of cyclooctene, polymer products with GPC-estimated molecular weights from 10 000 to 50 ,000 g/mol with expected polydispersity indices of approximately 2.

Addition of catalyst **2** to a solution of **1**-covered nanoparticles in CH_2Cl_2 resulted in a benzylidene exchange process similar to that described above. Upon addition of cyclooctene to these functional particles, ROMP was evidenced by the replacement of the original benzylidene resonances with a triplet at δ 19.28 ppm, characteristic of the chain-end ruthenium carbene (Figure

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(9) Fogg, D. E.; Radzilowski, L. H.; Blanski, R.; Schrock, R. R.; Thomas, E. L. *Macromolecules* **1997**, *30*, 417.

(10) Watson, K. J.; Zhu, J.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 462.

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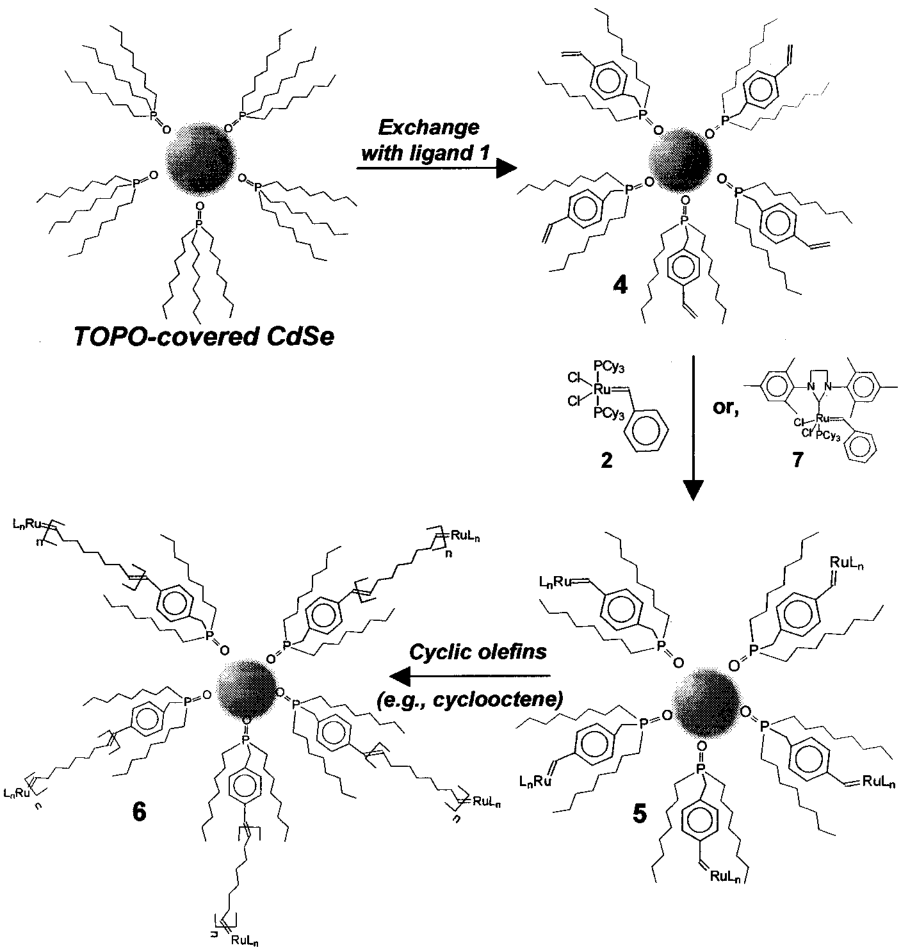
Scheme 2



2). These polymerizations could be performed at a variety of monomer and catalyst concentrations in CH_2Cl_2; typical experiments were conducted at 0.2 M monomer and 0.4 mM catalyst. Polymer formation was noted spectroscopically by the appearance of ^1H NMR signals at δ 5.4 ppm, characteristic of polycyclooctene unsaturation, and by the disappearance of the monomeric olefin resonances that were initially present at δ 5.6 ppm. The process as a whole is illustrated in Scheme 2, where the conventional TOPO-covered nanoparticles were transformed to coverage with ligand **1** (**4**), followed by addition of ruthenium catalyst to give "macroinitiator" **5**, and finally polymerization (of cyclooctene in Scheme 2) to give nanoparticle−polymer composite **6**.[13] Our illustration of macroinitiator **5** is purely schematic, in that instead of requiring fully catalyst-functionalized nanoparticles from the outset, our choice of **2** and **7** takes advantage of the chain-transfer capabilities of such catalysts, whereby the reactive ruthenium will locate unreacted double bonds in the system during the course of the polymerization. This appears to work well for providing full surface coverage, as ^1H NMR spectra of nanoparticle−polymer composite **6** show the decrease and eventual disappearance of vinyl signals from **2** at δ 6.7 ppm, and appearance of new signals at δ 6.10−6.40 ppm, for protons from the internal olefin attached to the aromatic ring in **6**. Furthermore, limiting the amount of catalyst makes its removal from the composite product feasible (or in some cases unnecessary) after polymerization.

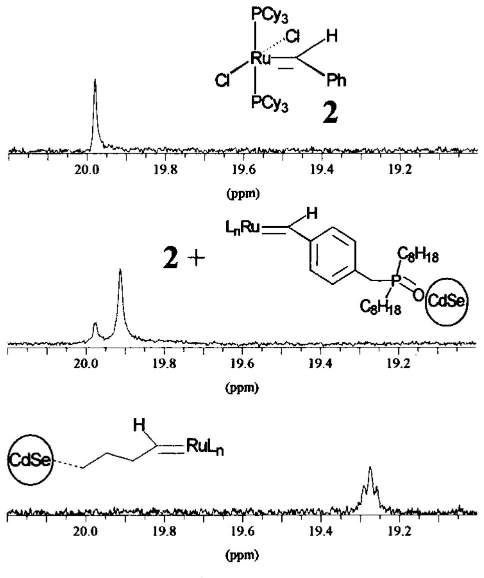


Figure 2. Selected region of ^1H NMR spectra showing the ruthenium benzylidene proton of compound **2** (top), **2** and metathesis exchange product (middle), and the CdSe−poly(cyclooctene) composite (bottom).

Our approach proved applicable to other cyclic olefin monomers. The process described above could be carried out when cyclooctene was replaced with dicyclopentadiene (**8**), *exo*-7-oxanorbornene-2,3-dicarboxylic anhydride (**9**), or *exo*-*N*-ethyl-7-oxanorbornene-2,3-dicarboxylimide (**10**). In all three cases, successful ring-opening metathesis polymerization from **1**-cov-

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[13] The core−shell composite **6** is interspersed with nonsurface bound polymer chains that initiate from the styrene byproduct of the metathesis exchange.

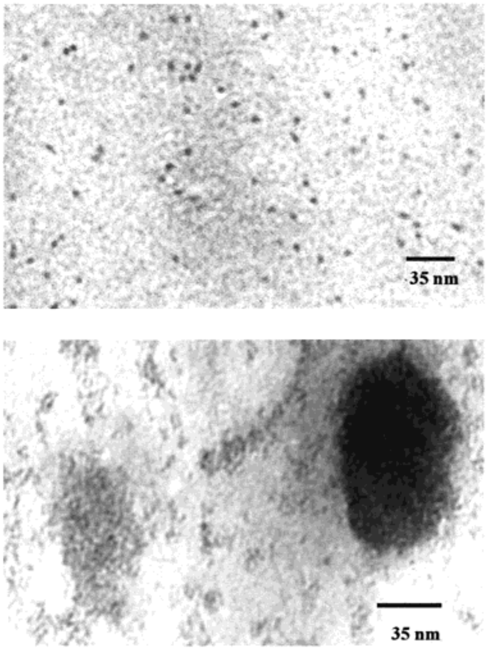

Figure 3. TEM micrographs of a thin film of CdSe−poly(cyclooctene) composite material from **1**-covered nanoparticles (top) and TOPO-covered nanoparticles (bottom).

ered nanoparticles catalyzed by **2** or **7** gave novel CdSe−polyolefin composites. In the case of dicyclopentadiene, a cross-linked network composite was obtained as a consequence of the difunctional nature of the monomer. With monomer **9** a composite material with anhydride functionalities along the polymer backbone was obtained, and use of **10** resulted in a soluble, processible material where the imide functionalities along the polymer backbone represent potential attachment sites for other functionality. This ability to incorporate CdSe nanoparticles into a broad range of polymers (semicrystalline from cyclooctene; network gels from dicyclopentadine; and functional materials from oxanorbornenes **9** and **10**) demonstrates the generality of the approach and should expand the scope of potential future technologies.

The CdSe−polymer composites prepared in this study afford optically clear solutions in organic solvents,[14] with absorption and photoluminescent emission profiles similar to those of the starting nanoparticles. UV−visible spectra of composite **6** in toluene show a broad absorption between 250 and 450 nm, due to a combination of nanoparticles and residual catalyst. Quenching the nanoparticle-initiated cyclooctene polymerization with ethyl vinyl ether[12b] was followed by slow addition of methanol to precipitate the polymer−nanoparticle composite and leave residual catalyst in solution. Alternatively, trace quantities (catalyst-to-monomer ratio ca. 1/5000) of the more active catalyst **7** (Scheme 2) were employed to give similar polymer−nanoparticle composites with negligible catalyst absorption. Both methods successfully afford the desired composites, but the process using **7** does not require catalyst removal in order to clearly observe nanoparticle luminescence.

The CdSe−poly(cyclooctene) composites could be solution or spin cast into thin, homogeneous films, and analyzed by TEM to reveal excellent particle dispersion in the poly(cyclooctene) matrix (Figure 3, top). As a result of effective surface coverage and the polymer growth process initiated from the nanoparticle surface, the particles in the composite product have a mean interparticle separation that is significantly greater than that observed in the starting material. Importantly, the value of ligand **1** as a functional phosphine oxide, with its simultaneous coordinative attachment to particles and covalent attachment to polymers, was confirmed by performing ROMP of cyclooctene in the presence of conventional TOPO-covered nanoparticles. These composites showed substantial particle aggregation (Figure 3, bottom). This is not surprising as in this latter case there is no chemical attachment between the particle and polymer, and the unchanged local environment of TOPO-covered particles limits severely their ability to disperse in the polymer film. Thus, it is clear that our growth method effectively prohibits such gross aggregation phenomena for cadmium selenide nanoparticles.

In summary, we have demonstrated the use of a new ruthenium-based olefin metathesis catalyst **3** for the preparation of novel CdSe−polymer composites. This growth method allows one to use simple, commercial monomers (in addition to specialty monomers) to prepare novel composite materials that retain the important property of nanoparticle dispersion in the product. This polymerization chemistry on CdSe demonstrates for the first time polymer growth radially outward from the CdSe nanoparticle surface, in a step toward a better understanding of the chemistry that will be compatible with nanoparticles of potential technological importance. We believe that the simplicity and generality of our method will allow for further development of a diverse collection of nanoparticle−polymer composites with a variety of solution and electronic properties.

Experimental Section

General. Selenium (99.999%), tri-*n*-octylphosphine (tech., 90%), and tri-*n*-octylphosphine oxide were purchased from Alfa Aesar. Hexylphosphonic acid (HPA) was prepared by a literature procedure,[15] or purchased from Organometallics, Inc. Cadmium oxide, 4-vinyl-(benzyl chloride), dibutyl phosphite, cyclooctene, and all other reagents were purchased from Aldrich. Tetrahydrofuran was purified by conventional distillation over sodium/benzophenone, and dichloromethane was distilled over calcium hydride. Ring-opening metathesis polymerization catalysts **2** and **7** were purchased from Strem. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker-Spectrospin 300. UV/visible spectra were recorded on a Hewlett-Packard 8453. Photoluminescence measurements were taken on a Perkin-Elmer LS50B (excitation 330 nm). Transmission electron microscopy (TEM) was performed on a JEOL 100CX microscope at 100 keV and 66 K magnification. TEM grids were purchased from Ted Pella, Inc. and consisted of 3−4 nm amorphous carbon film supported on a 400-mesh copper grid.

Preparation of *p*-Vinylbenzyl-DOPO (1). Sodium hydride (72 mg, 3.0 mmol) in THF (10 mL) was stirred at room temperature for 30 min. To this mixture was added a solution of di-*n*-octyl phosphine oxide (0.50 g, 3.0 mmol) in THF (15 mL). The mixture was stirred for 30 min, then a solution of 4-vinylbenzyl chloride (0.47 g, 3.0 mmol) in THF (5 mL) was added dropwise over 15 min. This mixture was stirred for 12 h at reflux. THF was then distilled off, and the solids were redissolved in CH_2Cl_2. The organic solution was then washed with water and brine, dried over $MgSO_4$, filtered, and concentrated to give a viscous liquid. This residue was crystallized from hexane to yield **1** (0.69 g, 62%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, 2H, aromatic), 7.21 (d, 2H, aromatic), 6.70 (dd, 1H, olefin), 5.70 (d, 1H, olefin), 5.22 (d, 1H,

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(14) With the exception of the insoluble networks from dicyclopentadiene.

(15) Andrianov, K. A.; Vasil'eva, T. V.; Demykina, T. K. *J. Gen. Chem. USSR* **1970**, *40*, 1565.

olefin), 3.10 (d, 2H, benzyl CH_2), 1.58 (br, 4 H, CH_2−P of *n*-octyl chains), 1.26 (br, 24 H), 0.88 (t, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 136.2, 131.9, 129.6, 126.5, 113.7, 36.3, 31.7, 30.9, 28.9, 27.7, 26.8, 22.6, 21.5, 14.0 ppm; ^{31}P (121 MHz, $CDCl_3$) δ 48.4 ppm; FTIR ν 2953, 2922, 2849, 1631, 1511, 1468, 1173, 1135, 988, 902, 864, 838, 721, 551, 471 cm^{-1}; HRMS calcd 390.3054, found 390.3013.

Preparation of 1-Covered CdSe Nanoparticles. TOPO-covered nanocrystals were prepared as described by Peng and co-workers,[6] then precipitated into anhydrous methanol and centrifuged. The supernate was discarded and the particles were dissolved in pyridine and allowed to stand at room temperature. The pyridine was partially removed under reduced pressure to give a viscous solution. The nanocrystals were precipitated into hexane and centrifuged. The supernate was discarded, and the precipitate (ca. 40 mg of CdSe nanocrystals) was stirred as a suspension in freshly distilled, dry THF. Compound **1** (ca. 300 mg) was added, and the suspension was stirred for several hours at 55 °C, during which time the mixture became homogeneous. Most of the THF was removed by distillation, and the remaining solution was twice precipitated with anhydrous methanol and centrifuged. The supernate was again discarded, and the **1**-covered nanocrystals were dissolved in freshly distilled, dry CH_2Cl_2 (ca. 2 mL).

Metathesis Reaction of 1 and Catalyst 2. A ^{1}H NMR spectrum was recorded of a solution of **2** (5 mg, 6 μmol) in $CDCl_3$ (0.8 mL). Compound **1** (4.7 mg, 12 μmol) was then added to the solution and allowed to react for 20 min; a ^{1}H NMR spectrum was then recorded to confirm successful carbene exchange: key benzylidene resonances at δ 19.97 (s, 1H), 19.92 (s, 1H). Addition of cyclooctene (0.11 g, 1.0 mmol) to this solution resulted in full conversion to polymer in approximately 1 h, as observed by ^{1}H NMR.

Example Preparation of a Poly(cyclooctene)−CdSe Composite. Poly(cyclooctene)−CdSe composites were prepared first by alkylidene exchange of **1**-covered nanoparticles with catalysts **2** or **7**, for example, by adding catalyst **2** (4 μmol) or catalyst **7** (0.3 μmol) to the CH_2Cl_2−nanocrystal solution prepared as described above; the exchange process was monitored by ^{1}H NMR spectroscopy as depicted in the text. This solution was shaken vigorously and allowed to stand for 30 min. Into this solution was added cyclooctene (0.11 g, 1.0 mmol), and the mixture was shaken occasionally over 2 h. Polymerization was terminated by addition of excess ethyl vinyl ether in CH_2Cl_2, and the product was precipitated by slow addition of methanol. The precipitate was dried under reduced pressure at room temperature, then dissolved in CH_2Cl_2. These CH_2Cl_2 solutions were used to spin and solution cast nanoparticle/polymer films, including those used for TEM analysis. The ^{1}H NMR spectrum of this composite material reveals the presence of polycyclooctene as major signals at δ 5.4 (multiplet), 2.0 (broad), and 1.3 (broad) ppm. No signals were present for the vinyl group of **1** (6.7 ppm), and a multiplet was found at 6.1−6.4 ppm, in the expected region for the protons of an olefin between a phenyl ring and an alkyl group, as in composite **6**.

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Supporting Information Available: Experimental procedures for composites prepared from monomers **8**−**10**, data on benzylidene exchange of **1** and **2**, and absorption and emission spectra of nanoparticles before and after polymerization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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