flavin group. The asymmetric induction seems to be induced by hydrophobic π–π stacking between the phenyl ring of the substrate and that of the catalyst to fix the direction of the substrate. Nucleophilic attack of the hydroperoxylflavin at the carbonyl group of the substrate occurs from the opposite side of the phenyl group of the substrate. Thus intramolecular rearrangement occurs antiperiplanar to the leaving group[3b] to give the corresponding optically active lactones with up to 74% ee. This is the first demonstration that organic chiral compounds can catalyze asymmetric Baeyer–Villiger reactions, and will become a trigger to provide future environmentally friendly, clean organocatalytic oxidation reactions.

In conclusion, we demonstrated that novel planar-chiral bisflavinium perchlorate 1 catalyzes the asymmetric Baeyer–Villiger reaction of cyclobutanones with hydrogen peroxide to give the corresponding optically active lactones with up to 74% ee. This is the first demonstration that organic chiral compounds can catalyze asymmetric Baeyer–Villiger reactions, and will become a trigger to provide future environmentally friendly, clean organocatalytic oxidation reactions.

Received: February 11, 2002 [Z18691]

[21] Control experiments show that HClO₄-catalyzed Baeyer–Villiger reaction of 2a in CF₃CH₂OH/MeOH/H₂O at −30 °C gave racemic 3a in 20% yield after 6 days.

Formation of High-Quality CdS and Other II – VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers**

W. William Yu and Xiaogang Peng*

Semiconductor nanocrystals are of great interest for both fundamental research and industrial development.[1, 2] The lack of adequate synthetic methods for nanocrystals of the desired quality is currently a bottleneck in this field.[3] The relatively successful approaches, including the organometallic approach[4–8] and its alternatives,[9–13] are exclusively performed in coordinating solvents. Evidently, only a few compounds can act as the coordinating solvents,[11] and this makes it extremely challenging to identify a suitable reaction system for growing high-quality nanocrystals in most cases. Here we show that noncoordinating solvents not only are compatible with the synthesis of semiconductor nanocrystals, but also provide tunable reactivity of the monomers by simply varying the concentration of ligands in the solution. The tunable reactivity of the monomers provides a necessary balance between nucleation and growth, which is the key for control over the size and size distribution of the resulting nanocrystals.[5] In practice, such tunability has great potential to promote the synthesis of various semiconductor nanocrystals to the level of that of the well-developed CdSe.
nanocrystals in coordinating solvents. A successful synthetic scheme for high-quality CdS nanocrystals is demonstrated here.

The noncoordinating solvent used in this study was octadecene (ODE), which is a liquid at room temperature and boils at about 320 °C. Oleic acid, a natural surfactant, was chosen as the ligand for stabilizing the nanocrystals and the cationic precursors. For the synthesis of CdS, the precursors were CdO and elemental sulfur, two naturally occurring minerals. For the synthesis of CdS nanocrystals (for details, see Experimental Section), CdO was dissolved in ODE by reaction with oleic acid at elevated temperature. Into this hot solution, a room-temperature solution of elemental sulfur in ODE was injected. The reaction was monitored by UV/Vis absorption and photoluminescence (PL) spectroscopy by taking aliquots from the reaction flask.

The power of noncoordinating solvents is demonstrated by the results shown in Figure 1. All reactions in Figure 1 were performed under identical conditions, except for the concentration of oleic acid in the reaction mixture. With pure oleic acid as coordinating solvent, only a small amount of bulk CdS particles were observed. As the concentration of oleic acid in ODE decreased, the growth rate of the nanocrystals slowed down systematically, and the size distribution of the resulting nanocrystals became significantly narrower at the focus of the size distribution, as indicated by the sharpness of the first absorption peak of the sharpest spectrum in each series.

Similar results were obtained for the synthesis of ZnSe and CdSe nanocrystals in ODE with oleic acid as ligand. ZnSe nanocrystals, regardless of their size, cannot be formed in pure oleic acid, pure trioctylphosphane oxide (TOPO), or a mixture thereof as coordinating solvent. This even holds for the traditional organometallic approach. However, using a dilute solution of oleic acid in ODE, we observed the formation of ZnSe nanocrystals with a decent size distribution. In pure fatty acids or mixtures thereof with TOPO, it is not practical to synthesize CdSe nanocrystals with relatively small sizes (<4 nm). With ODE as noncoordinating solvent and an appropriate amount of oleic acid as ligand, the size of CdSe nanocrystals can range from approximately 1.5 to 20 nm in a controllable fashion.

The influence of the concentration of oleic acid on the growth kinetics of CdS nanocrystals (Figure 1) and of other types of semiconductor nanocrystals is dramatic. This influence is the result of the tuned reactivity of the cationic monomers in the noncoordinating solvent, where the term “cationic monomer” refers to all cadmium or zinc species in solution that are not in the form of nanocrystals. A reaction mixture for the synthesis of CdS in ODE after a given reaction time was separated to two fractions by extraction with CHCl3/CH3OH (1:1). Apparently, the CdS nanocrystals are only soluble in the ODE phase, and oleic acid and cadmium oleate are both extracted into the CHCl3/CH3OH phase. This separation was confirmed by UV/Vis and FTIR measurements (see Figure 2, left and Supporting Information). After this separation, the concentration of unconverted cadmium oleate in the reaction solution was determined by atomic absorption spectroscopy (Figure 2, right). The concentration of cadmium monomer in the solution dropped very quickly during the first 20 s, and the rate of this depletion increased with decreasing oleic acid concentration (Figure 2, right). From the spectra in Figure 1, one can find that the average size of the nanocrystals about 20 s after the injection decreases systematically with decreasing initial oleic acid concentration.

In contrast, the depletion rate of the monomers did not change much with a different initial oleic acid concentration after the initiation stage of the reactions, although the remaining monomer concentra-
concentration was higher for the reactions with a higher oleic acid concentration. Likely, this is caused by two conflicting factors. In comparison to a reaction with a lower ligand concentration, the reactivity of the monomers of a given reaction was lower but the remaining concentration of the monomers was higher.

The influence of the ligand concentration in controlling the size and size distribution of the nanocrystals is dramatic (Figure 1). According to current understanding, control of the size distribution of growing colloidal nanocrystals is achieved by a balance between nucleation and growth. A successful synthetic scheme should start with a fast and short nucleation period, which is followed by a growth stage without either prolonged nucleation or ripening, which is referred as “focusing of size distribution”. If too many nuclei were formed in the initial nucleation period, the remaining monomers would not be sufficient to promote the focusing of size distribution for a sufficient time, and this would result in an undesired Ostwald ripening or defocusing of size distribution. If too few nuclei formed, the growth reaction would be too fast to be controlled to reach the desired size and size distribution. To achieve this essential balance between nucleation and growth, a nearly continuous tunable reactivity of the monomers is desirable. As discussed above, such tunability can be readily achieved by simply altering the ligand concentration in a noncoordinating solvent. This tunability may indicate that the cadmium monomers in the solution at elevated temperatures are not simply cadmium oleate. The number of “nearby” ligands for each cadmium ion may strongly depend on the concentration of the ligands in the bulk solution. Consequently, the reactivity of those cadmium complexes at elevated temperatures varies with the ligand concentration in solution.

To our knowledge, the UV/Vis absorption and photoluminescence (PL) spectra shown in Figure 3 are among the sharpest for CdS nanocrystals reported[8, 15, 16] and this indicates a superior size distribution of the nanocrystals formed in ODE. The achievable size range is also plausible when compared to the existing synthetic schemes.[8, 15, 16] The approach with a noncoordinating solvent presented here can reproducibly and controllably generate CdS nanocrystals in almost the entire quantum confined size regime (ca. 1–6 nm), with the first exciton absorption peak from 305 nm (likely a magic size, see Figure 1) to about 440 nm. The PL of the CdS nanocrystals is dominated by the band-edge emission, except for those smaller than about 2 nm. Transmission electron microscope (TEM) measurements (Figure 4) confirmed that the size distribution of the as-prepared CdS nanocrystals was nearly monodisperse in the entire size range mentioned above, with a relative standard deviation of 5–15% without any size sorting. The diffraction pattern seems to combine that of wurtzite nanocrystals with one or more zinc blende stacking faults along the c axis.[8] Importantly, the synthesis can also be performed with the reaction system open to air without deteriorating the quality of the nanocrystals (see Supporting Information).

In conclusion, the temporal course of the nucleation and growth of semiconductor nanocrystals can be tuned by simply changing the concentration of the ligands in a noncoordinating solvent. Such flexibility is impossible for a synthesis performed in coordinating solvents. Appropriate reactivity of the monomers, manipulated by varying the ligand concentration in noncoordinating solvent, led to a balance between the two conflicting requirements of a successful synthetic scheme: a fast but short nucleation stage and a slow but long growth stage without Ostwald ripening.[5] Although this work focused on the synthesis of II–VI semiconductor nanocrystals in ODE, we believe ODE will not be a unique noncoordinating solvent, and other such solvents should be suitable for the synthesis of different types of colloidal nanocrystals. The introduction of noncoordinating solvents further enhances the possibility of implementing green-chemical principles into the design of synthetic schemes for colloidal nanocrystals, which
may become significant for industrial production of those novel materials.\[^{[3]}\] As demonstrated above, the procedure and the chemicals used for the synthesis of high-quality CdS nanocrystals are simple, safe, and inexpensive in comparison to those reported previously.\[^{[8,15,16]}\]

**Experimental Section**

Typically, a mixture (4 g in total) of CdO (0.0128 g, 0.10 mmol), oleic acid (0.30–21.2 mmol), and technological-grade ODE (Aldrich) was heated to 300 °C. A solution of sulfur (0.0016 g, 0.05 mmol) in ODE was swiftly injected into this hot solution, and the reaction mixture was allowed to cool to 250 °C for the growth of CdS nanocrystals. The synthesis can be carried out under argon or open to air. Aliquots were taken at different time intervals, and UV/Vis and PL spectra were recorded for each aliquot. XRD and TEM measurements were also performed to characterize the crystallinity, size, and size distribution of the resulting crystals. The size-distribution diagrams were obtained by measuring about 500 individual CdS nanocrystalline particles on enlarged photographs. All the measurements were performed on the original aliquots without any size sorting. The unconsumed cadmium precursor was separated from the nanocrystals by the repeated extraction of the reaction aliquots with an equal volume of CHCl\textsubscript{3}/CH\textsubscript{3}OH (1:1). The extraction process was monitored by a UV/Vis absorption spectrophotometer. The size of the resulting nanocrystals were determined by TEM measurements and literature data on size versus the position of the first sorption peak.\[^{[6,14]}\] The characterization and sample preparation of the nanocrystals, including X-ray diffraction, TEM, PL, and UV/Vis, were reported in a previous paper.\[^{[14]}\] The size distribution was also determined by using the method reported in ref. \[^{[14]}\] The CdSe and ZnSe nanocrystals were synthesized in a similar fashion; the selenium precursor was a solution of selenium/tributylphosphane (1:1) in ODE. The unreacted cadmium precursor was separated from the CdSe and ZnSe nanocrystals by the repeated extraction of the reaction aliquots with an equal volume of CHCl\textsubscript{3}/CH\textsubscript{3}OH (1:1). The extraction process was monitored by a UV/Vis absorption spectrophotometer. The size of the resulting nanocrystals were determined by TEM measurements and literature data on size versus the position of the first sorption peak.\[^{[6,14]}\] The characterization and sample preparation of the nanocrystals, including X-ray diffraction, TEM, PL, and UV/Vis, were reported in a previous paper.\[^{[14]}\] The size distribution was also determined by using the method reported in ref. \[^{[14]}\] The CdSe and ZnSe nanocrystals were synthesized in a similar fashion; the selenium precursor was a solution of selenium/tributylphosphane (1:1) in ODE.

Received: January 31, 2002 [Z18622]


**An Umpolung Approach to cis-Hyponitrite Complexes**

Navamoney Arulsamy, D. Scott Bohle,* Jerome A. Imonigie, and Seth Levine

Dedicated to Professor Karl Wieghardt
on the Occasion of his 60th Birthday

The reductive dimerization of nitric oxide to give nitrous oxide is an important process both in the remediation of nitrogen-oxide pollutants in flue and exhaust gases by heterogeneous platinum metals,\[^{[1]}\] and in the use of the oxyanions of nitrogen as terminal electron acceptors by dissimilatory bacteria.\[^{[2]}\] In these transformations the key step is the formation of the nitrogen–nitrogen double bond, and here the frequently proposed mechanism is the stereospecific dimerization of nitroxyl, NO\textsubscript{2}, to give cis hyponitrite, followed by elimination of nitrous oxide, [Eq. (1)].\[^{[3]}\]

\[
2 \text{NO}^- \longrightarrow \text{O}_2^= \text{N}^- \text{N}^= \text{H}^+ \rightarrow \text{N}_2\text{O} + \text{OH}^- \quad (1)
\]

Unlike \textit{trans} hyponitrite, for which there is an extensive and well established structural,\[^{[4]}\] mechanistic,\[^{[5–8]}\] and derivative chemistry,\[^{[9]}\] our knowledge of \textit{cis} hyponitrite is sparse. Although an elegant spectroscopic and structural study of sodium \textit{cis} hyponitrite,\[^{[10,11]}\] derived from the solid-state reaction of sodium oxide and nitrous oxide, established a new benchmark for this area, the reactivity of the free or coordinated diamin remains vaguely outlined. Thus key aspects of the kinetics and mechanism of the decomposition of \textit{cis} hyponitrite, its coordination chemistry, and alkylation remain unknown. Furthermore, there is only a solitary structurally characterized complex of a chelated mononuclear \textit{cis} hyponitrite, [Pt(\textit{η}^2-O\textsubscript{2}N\textsubscript{2})(PPh\textsubscript{3})\textsubscript{2}], which results from the equally unique oxidative coupling of two nitric oxides by [Pt(PPh\textsubscript{3})\textsubscript{4}].\[^{[12–18]}\] Related reactions for different late transition metals are thought to give \textit{trans}-hyponitrite complexes.\[^{[19–21]}\] Herein we describe: 1) a new general method for the introduction and stabilization of \textit{cis} hyponitrite in the coordination sphere of a metal, 2) the structure of one of these complexes, [Ni(\textit{η}^2-O\textsubscript{2}N\textsubscript{2})(dpfp)], (dpfp = 1,1’-bis(diphenylphosphanyl)ferrocene), and 3) the reactivity of these new \textit{cis}-hyponitrite complexes.

We recently described the synthesis of a new class of diazeniumdiolates, R\textsubscript{2}N\textsubscript{2}O\textsubscript{2}, from the base-mediated condensation of 2,4,6-trisubstituted phenols with nitric oxide.\[^{[22]}\] In the course of characterizing one of these derivatives, with R = OMe, I, we observed rapid acid-promoted stoichiometric