

Homogeneously-Alloyed CdTeSe Single-Sized Nanocrystals with Bandgap Photoluminescence

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Supporting Information

1. Observation of ternary CdTeSe MSQDs, and temporal evolution of their optical properties

It has been widely accepted that, the most direct identification of MSQDs during following reaction kinetics by optical properties measurements is to observe stable (no red-shift during “growth”), persistent, and isolated peak in absorbance spectra during the reaction,¹⁻¹² whilst regular QDs growth normally features continuous and controllable absorbance red-shift over time during the reaction. **Figure S1** shows, fascinatingly, the reaction gave two MSQDs ensemble, one with absorbance persistently at 428 nm and the other with lowest absorbance band stably at 520 nm. The first MSQDs ensemble, grown from 120 °C up to 160 °C, has absorbance and emission characteristics resembling binary CdTe MSQD Family 428,¹² while the second MSQDs ensemble at 520 nm is an unprecedented, different from any reported binary MSQDs under the similar synthetic strategies (see Figure S1 and S2 for comparison).^{11,12} In addition, ¹¹³Cd CP/MAS and HPDEC solid-state NMR spectra have confirmed that this ensemble at 428 nm is actually binary CdTe Family 428, as it only contains Cd and Te without trace of Se contribution. This is interesting, as it seems only CdTe was produced at relatively low temperature when the both precursors TOPSe and TOPTe were available. As a matter of fact, it has been demonstrated before by Nie group and Cao group independently that TOPTe is more reactive than TOPSe, and the production rate of CdTe is significant faster than CdSe.^{13,4} Our experimental observation exactly supports their conclusion. In addition, MSQDs ensemble CdTe 428 is not thermally stable either at temperature higher than 160 °C, from our separate investigation,¹² thus were broken down and allowed the second MSQDs, a ternary ensemble, in

this reaction at 520 nm to appear. It is noteworthy that Family 524 is fairly stable, without any absorbance and emission redshifts under continuous heating at 180 °C for up to 1 hour or even higher temperature up to 220 °C.

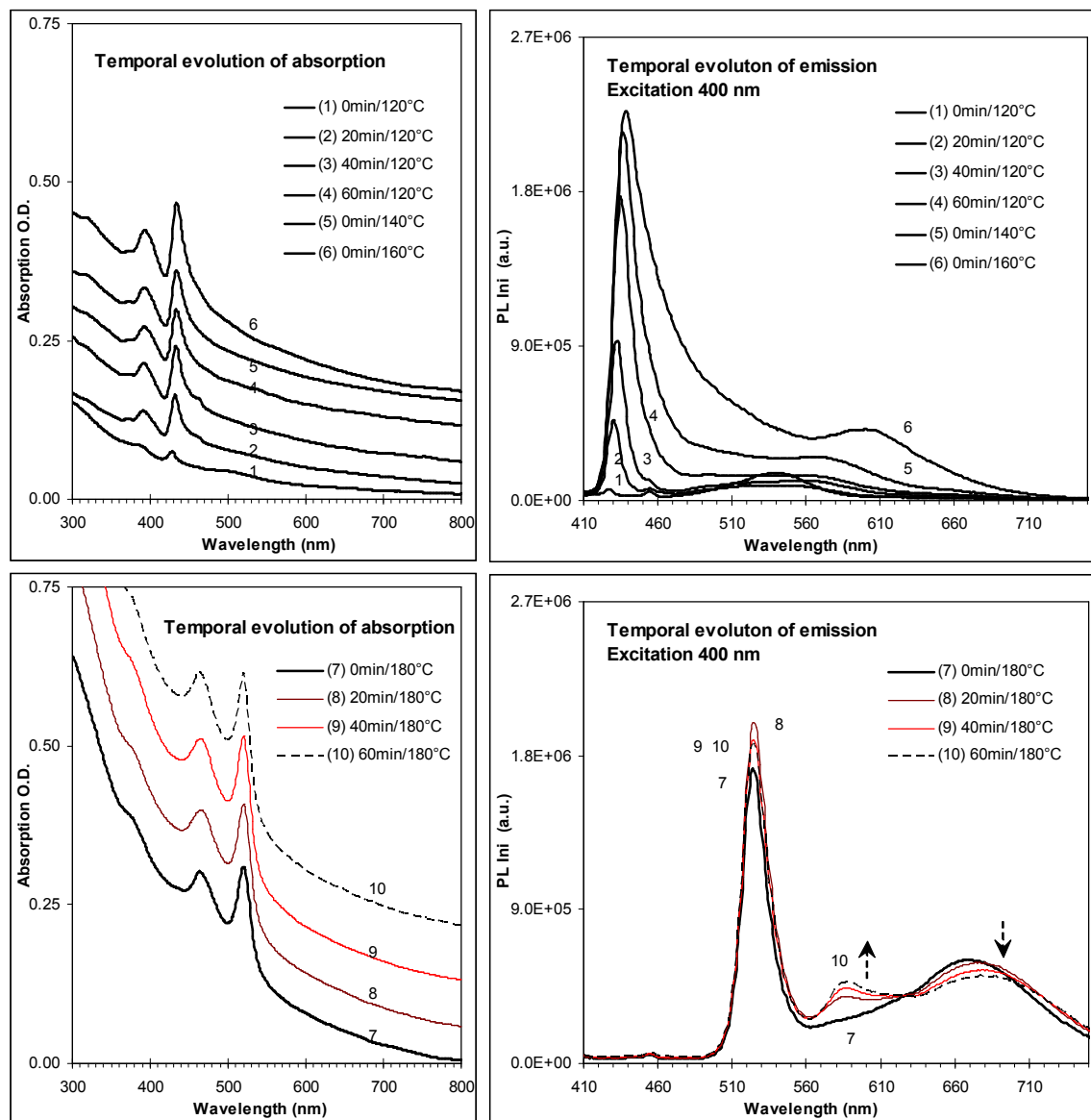


Figure S1. Temporal evolution of the optical properties of the as-synthesized nanocrystals from one synthetic batch with octanoic acid as the capping ligand and the feed molar ratios of 1acid-to-1Cd and 8Cd-to-1Te-to-1Se; the growth periods and temperature are indicated. The as-synthesized nanocrystals were dispersed in toluene. The absorption (**top-left**) and emission (**top-**

right) spectra on the top highlight the presence of CdTe MSQD Family 428 before 180 °C, and the absorption (**bottom-left**) and emission (**bottom-right**) spectra on the bottom highlight the presence of CdTeSe MSQD Family 524 at 180 °C. The examples of the synthesis of CdSe MSQD Family 395 and 463, and CdTe MSQD Family 428 from the other two previous synthetic batches for binary MSQDs are illustrated in Figure S2 for comparison.^{11,12}

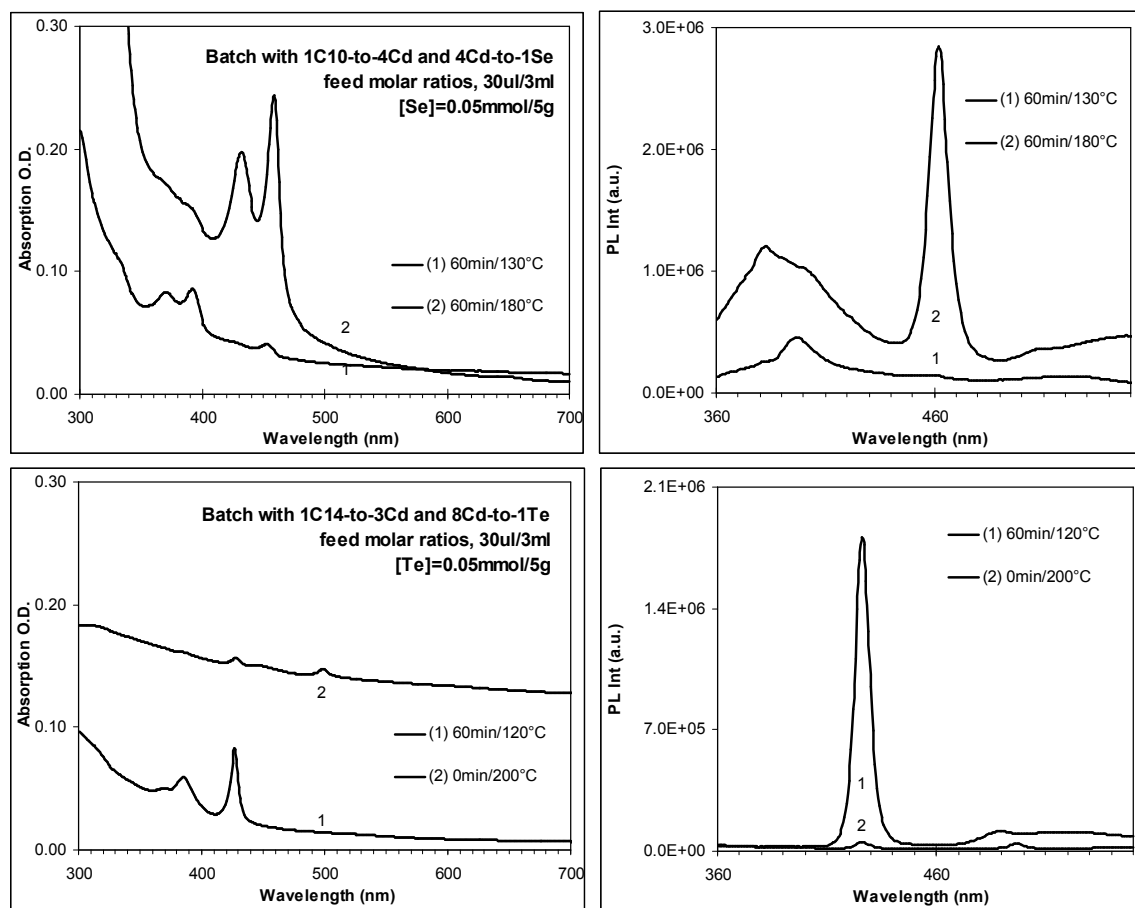


Figure S2. Absorption (**top-left**) and emission (**top-right**) spectra of CdSe MSQDs from one synthetic batch with synthetic parameters indicated, and absorption (**bottom-left**) and emission (**bottom-right**) spectra of CdTe MSQDs from another synthetic batch with synthetic parameters indicated in the figure. The growth periods and temperature are also labeled. It is clear that CdSe Family 395 grew first at 130 °C and then disappeared, while Family 463 grew at 180 °C. Also, CdTe Family 428 grew at 120 °C and then disappeared at 200 °C, while Family 500 grew.^{11, 12} It is noteworthy that MSQDs do not grow anymore after their formation; they stay or decompose with longer growth periods and higher reaction temperature. For the present

synthesis of CdTeSe MSQDs, as shown in Figure S1, CdTe Family 428 appeared first at 120 °C due to the relatively high reactivity of Te, as compared with that of Se.^{13,14} However, due to the thermal stability, CdTe Family 428 decomposed at ca. 180 °C, where the formation of CdTeSe MSQDs started as shown in Figure S1.

2. Solid-NMR ^{13}C CP/MAS of CdTeSe MSQDs

The ^{13}C CP/MAS spectra (**Figure S3**) with and without dipolar dephasing provide information on the dynamics of the capping ligands. The dipolar dephased spectrum (a) shows non-protonated carbons and any protonated carbons which are undergoing rapid motion show with reduced intensity. The fact that some of the CH_2 resonances of the octyl chain do not appear in the dipolar dephased spectrum (a) therefore indicates that these are static. At the same time some of the CH_2 must be dynamic. The explanation is that the carboxylate group is attached firmly to the surface and this and several of the CH_2 closest to it are immobilized, whereas CH_2 further along the chain have more freedom to move. The fact that the ligand is firmly attached then allows ^1H - ^{113}Cd cross-polarization from the static CH_2 groups to the Cd.

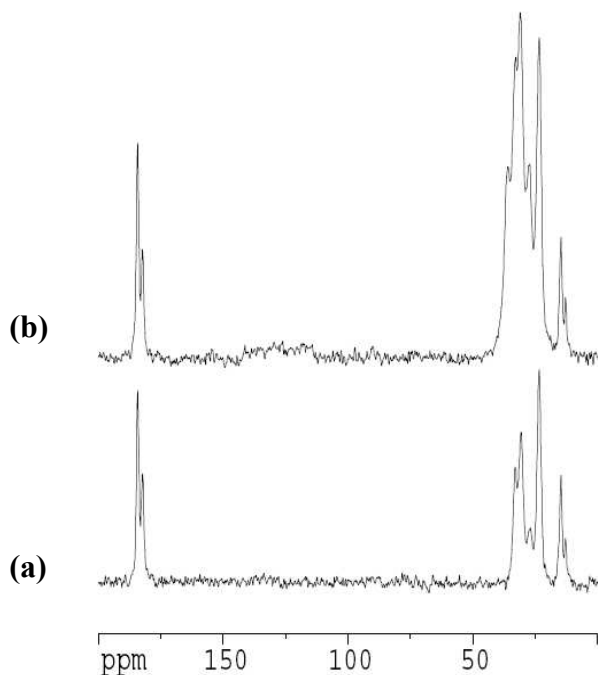


Figure S3. ^{13}C CP/MAS NMR spectra of the CdTeSe 524 MSQD ensemble with (a) and without (b) dipolar dephasing, indicating that carboxylate ligands are anchored on the surface.

3. EDX Characterization

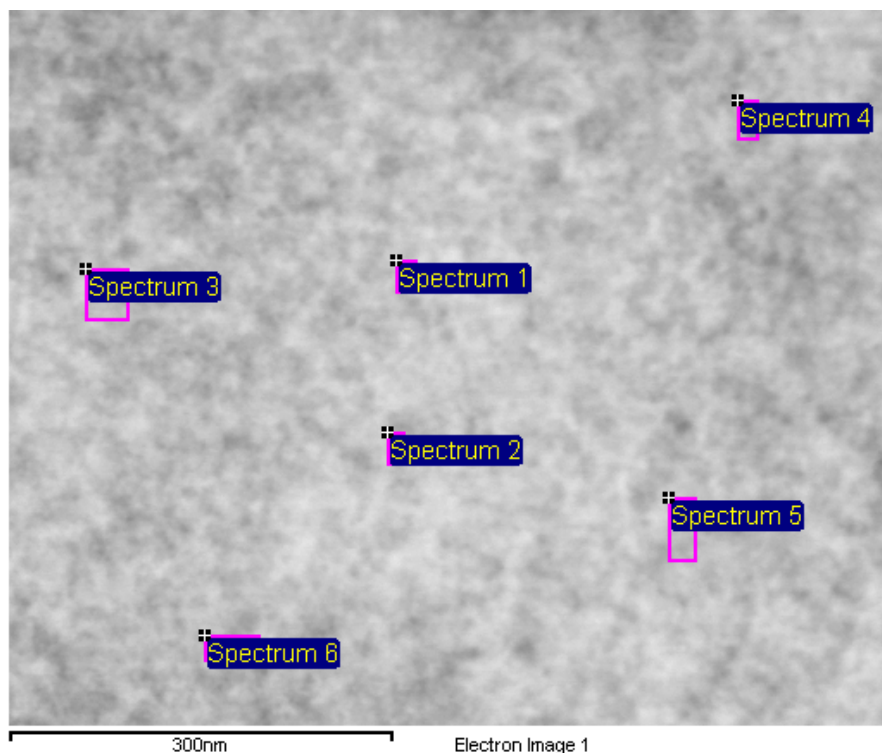


Figure S4. An electron image with the indication of the 6 different areas for our EDX analysis. A representative EDX spectrum was given in main text as Figure 4. The results are shown in **Table S1**.

Table S1. Atomic composition of the CdTeSe MSQD sample (with the results in atomic%) analyzed by the EDX spectra.

Spectrum	In stats.	Se	Cd	Te
Spectrum 1	Yes	22.29	54.73	22.98
Spectrum 2	Yes	22.44	56.77	20.79
Spectrum 3	Yes	21.35	56.67	21.98
Spectrum 4	Yes	21.37	56.15	22.49
Spectrum 5	Yes	23.54	53.89	22.57
Spectrum 6	Yes	21.80	55.62	22.58
Mean		22.13	55.64	22.23
Std. deviation		0.83	1.14	0.78
Max.		23.54	56.77	22.98
Min.		21.35	53.89	20.79

4. Transmission Electron Microscopy (TEM)

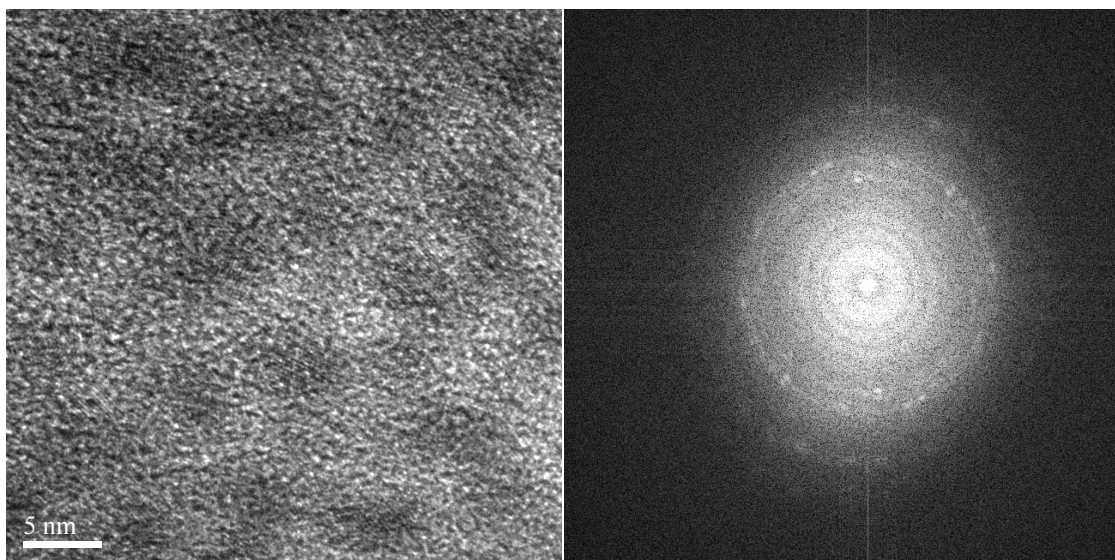


Figure S5. One HRTEM image (left) and one electron diffraction pattern derived (right) of purified ternary F524 magic-sized nanocrystals.

5. DOSY NMR for Size Determination

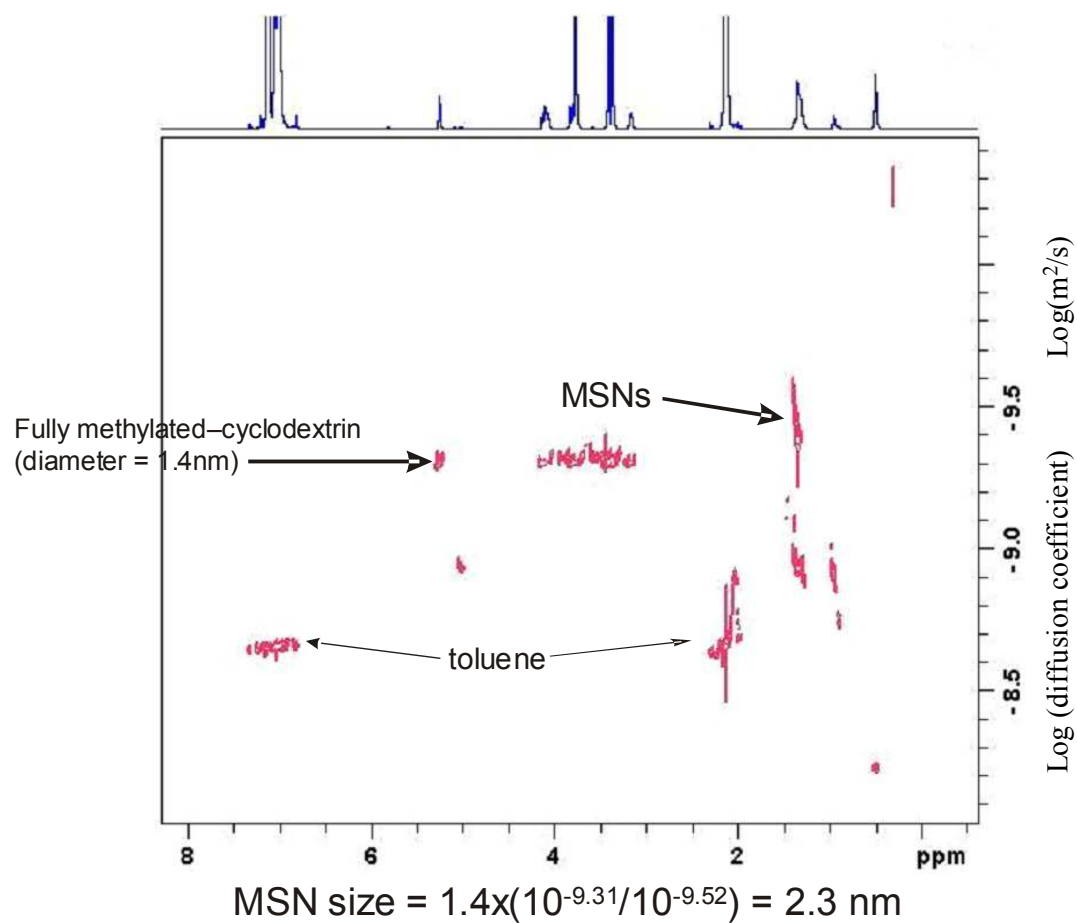


Figure S6. DOSY NMR determines the size of MSQDs to be ca $2.3(\pm 0.5)$ nm in diameter. Right y axis is log (Diffusion Coefficient) and x axis is ^1H chemical shift in ppm. The diffusion coefficient of the MSQDs is $10^{-9.31} \text{ m}^2/\text{s}$.

References

1. Platschek, V.; Schmidt, T.; Lerch, M.; Muller, G.; Spanhel, L.; Emmerling, A.; Fricke, J.; Foitzik, A. H.; Langer, E. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1998**, *102*, 85.
2. Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 3343–3353.
3. Cumberland, S. L.; Hanif, K. M.; Javier, A.; Khitrov, G. A.; Strouse, G. F.; Woessner, S. M.; Yun, C. S. *Chem. Mater.* **2002**, *14*, 1576–1584.
4. Pradhan, N.; Xu, H.; Peng, X. *Nano Lett.* **2006**, *6*, 720–724.
5. Vossmeier, T.; Katsikas, L.; Giersig, M.; Popovic, I. G.; Diesner, K.; Chemseddine, A.; Eychmueller, A.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 7665–7673.
6. Kudera, S.; Zanella, M.; Giannini, C.; Rizzo, A.; Li, Y.; Gigli, G.; Cingolani, R.; Ciccarella, G.; Spahl, W.; Parak, W. J.; Manna, L. *Adv. Mater.* **2007**, *19*, 548–552.
7. Dagtepe, P.; Chikan, V.; Jasinski, J.; Leppert, V. J. *J. Phys. Chem. C* **2007**, *111*, 14977–14983.
8. Soloviev, V. N.; Eichhofer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2001**, *123*, 2354–2364.
9. Bowers, M. J.; McBride, J. R.; Rosenthal, S. J. *J. Am. Chem. Soc.* **2005**, *127*, 15378–15379.
10. Evans, C. M.; Guo, L.; Peterson, J. J.; Maccagnano-Zacher, S.; Krauss, T. D. *Nano Lett.* **2008**, *8*, 2896–2899.
11. Ouyang, J.; Zaman, Md. B.; Yan, F. J.; Johnston, D.; Li, G.; Wu, X.; Leek, D.; Ratcliffe, C. I.; Ripmeester, J. A.; Yu, K. *J. Phys. Chem. C* **2008**, *112*, 13805–13811.
12. Wang, R.; Yu, K. *Chem. Commun.*, submitted, **2008**.
13. Bailey, R. E.; Nie, S. *J. Am. Chem. Soc.* **2003**, *125*, 7100–7106.
14. Yang, Y. A.; Wu, H.; Williams, K. R.; Cao, Y. C. *Angew. Chem. Int. Ed.* **2005**, *44*, 6712 – 6715.