

Nanoparticles

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Stabilization of High Oxidation State Upconversion Nanoparticles by N-Heterocyclic Carbenes

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Abstract: The stabilization of high oxidation state nanoparticles by N-heterocyclic carbenes is reported. Such nanoparticles represent an important subset in the field of nanoparticles, with different and more challenging requirements for suitable ligands compared to elemental metal nanoparticles. N-Heterocyclic carbene coated NaYF₄:Yb,Tm upconversion nanoparticles were synthesized by a ligand-exchange reaction from a well-defined precursor. This new photoactive material was characterized in detail and employed in the activation of photoresponsive molecules by low-intensity near-infrared light ($\lambda = 980$ nm).

Nanoparticles (NPs) have gained major importance during the last decade, particularly in the fields of organometallic drugs, materials, and catalysis.^[1] The required stabilization of the NPs, a key challenge in this research field, is usually achieved by ligands such as thiols, phosphines, carboxylates, and thioethers.^[2] N-Heterocyclic carbenes (NHCs), which are well-established ligands for organometallic chemistry,^[3] are an emerging ligand class for the stabilization of NPs.^[4-6] Various NHC designs have been employed for the stabilization of elemental metal NPs over several months,^[7] in ionic liquids,^[8] in water,^[9] under physiologically relevant conditions,^[10] and recently as bidentate ligands.^[11] Surprisingly, NHCs have so far not been used as ligands for oxidized transition-metal NPs such as metal oxides and fluorides,^[12] a significant subgroup of metal-based NPs (Figure 1).^[13] Comparing the electronic and material properties of elemental versus oxidized metal NPs, the higher electronic demand of the metal in oxidized NPs is evident and requires different characteristics of the stabilizing ligand compared to elemental metal NPs. As a consequence of the electron-poor character of the oxidized metals, the ligand used for such NPs should be an excellent donor. In addition, the formation of a strong bond between the ligand and the metal is desirable for the

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Figure 1. Comparison of NHC-stabilized elemental and oxidized state metal NPs.

generation of air- and moisture-stable NPs. Both requirements are fulfilled by NHCs for transition-metal complexes. Therefore, NHCs were envisioned to be suitable ligands for such NPs. A particularly interesting type of oxidized metal NPs are so-called upconversion nanoparticles (UCNPs), which are capable of emitting UV light under irradiation with near-infrared (NIR) light by the absorption of two or more photons.^[14] Consequently, UCNPs offer a broad spectrum of applications based on an external photostimulus, such as photoswitches, photocleavable groups for drug release, imaging, and sensing.^[15]

To probe the possibility of stabilizing UCNPs with NHCs, NaYF₄:Yb,Tm UCNPs were chosen as model particles and synthesized with oleic acid (OA@UCNPs) as the ligand.^[16] For the NHCs, a design with two small methyl substituents at the nitrogen atom (to reduce the steric bulk directed towards the metal surface) and two undecyl chains in the backbone (to stabilize the NPs through steric repulsion) was selected, namely C₁₁-IMe. Additional advantages of this design are the apolar coating around the NP, which leads to less photoquenching at the NP surface, and the synthetic utility of the NHC. The presence of such a synthetic handle in the backbone enables functionality to be easily installed prior to or after ligand exchange, which cannot be done with oleic acid. By using this approach, an azide-functionalized NHC was employed to install a photoactive azobenzene close to the surface. The preparation of the corresponding C_{11} -IMe@UCNPs (Figure 1, right) was achieved by a ligandexchange reaction under anhydrous conditions starting from OA@UCNPs and the in situ generated free NHC by using a slightly modified procedure relative to that previously reported by Chechik and co-workers for metal NPs.^[4b] After precipitation with acetonitrile, centrifugation, and subsequent washing with acetonitrile, pure C11-IMe@UCNPs were obtained and could be redispersed in toluene or chloroform. It is important to note that other NHC ligands lacking the long alkyl chains for steric repulsion (IMe) or with increased steric bulk at the nitrogen atom (C11-IPr) resulted in irreversible precipitation or precluded ligand exchange. This finding is in agreement with our previous report, thus underlining the key features of the design.^[7] ¹H and ¹³C NMR spectroscopy was employed (Figure 2) to assess if

C₁₁-IMe-HI



Figure 2. ¹H (top) and ¹³C NMR spectra (bottom). Comparison of the ligand precursor C11-IMe-HI, OA@UCNPs, and C11-IMe@UCNPs. In the bottom spectra, ¹³C-enriched C₁₁-IMe-HI was used.

the ligand exchange completely replaces the precursor ligand and whether the NHC indeed binds through the carbene carbon atom (and not through electrostatic interactions of the reprotonated NHC). Indeed, complete ligand exchange was observed after stirring the reaction mixture overnight. Neither the olefinic protons from oleic acid nor the acidic imidazolium proton could be detected and a new broad signal appeared around 4 ppm, which corresponds to the methyl group on the NHC nitrogen atom.

In addition, the two undecyl chains in the backbone give rise to a broad signal between 0.5 and 1.5 ppm. All the signals are significantly broadened due to the proximity to the NP surface and the, therefore, limited degree of rotational and translational freedom. The ¹³C NMR spectra of the same C₁₁-IMe@UCNPs stabilized by ¹³C-labeled NHCs revealed a carbene signal around 170 ppm, which is about 20-25 ppm lower compared to known NHC-yttrium complexes (190.3 and 194 ppm) and about 33 ppm higher than the NHC salt (136.9 ppm).^[17] The width of the ¹³C carbene signal was the same as observed in previous studies.^[7,9,11]

PFG-NMR studies were conducted to verify the binding and the proximity between the NHC and UCNP surface. It was found that the unbound NHC salt-an air- and moisturestable NHC model—at $5.6 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ and free OA at $6 \times$ $10^{-10} \,\mathrm{m^2 s^{-1}}$ have a diffusion coefficient that is two magnitudes higher than their NP-bound versions. The NP-bound OA had a diffusion coefficient of $4 \times 10^{-12} \text{ m}^2 \text{s}^{-1}$ and the NP-bound NHC $5.2 \times 10^{-12} \text{ m}^2 \text{s}^{-1}$. This observation strongly supports the binding of the NHC to the UCNPs, as binding to the UCNP slows down the diffusion (see the Supporting Information).

Further control experiments were performed to distinguish between carbene binding and an electrostatic interaction. The addition of C₁₁-IMe-HI directly to the dispersion of OA@UCNPs in toluene led to a ligand exchange occurring, but the NMR spectra showed a signal for the acidic hydrogen atom of the NHC salt, that is, different from the spectrum of C₁₁-IMe@UCNPs. In this case the UCNP stabilization likely occurs by an electrostatic interaction of the NHC salt with the NP surface. The use of C₁₁-IMe-MeI, which contains a methyl group instead of an acidic hydrogen atom in the C2-position, led to an exchange but, in contrast to C11-IMe@UCNPs, only traces of poorly redispersable NPs were obtained. Presumably the electrostatic interaction between C₁₁-IMe-MeI and the UCNP is very weak. These results were confirmed when the cationic surfactant CTAB was employed instead of the NHC salt, which resulted in only the free surfactant being isolated and strongly supports the C₁₁-IMe-carbene binding.

Additional TGA measurements with OA@UCNPs and C11-IMe@UCNPs revealed that the NHC started to dissociate from 250°C, whereas OA@UCNPs dissociated at temperatures as low as 100 °C (see the Supporting Information). These results are consistent with a covalent bond between the NHC and the UCNP, not with an electrostatic interaction. The organic content was found to be 29% for OA@UCNPS and 36% for C₁₁-IMe@UCNPs, which is in good agreement to reported NHC-stabilized Pd NPs.^[7] Based on these results, and assuming the UCNP to have the same density as NaYF₄, the number of C₁₁-IMe ligands on one UCNP was calculated to be between 1339 and 1476.^[18] For OA, the number of ligands was calculated to be between 1398 and 1536 (see the Supporting Information), which leads to the conclusion that roughly one OA is replaced by one C_{11} -IMe.

XPS analysis was conducted to further probe the binding of the NHC to the UCNP. XPS is an effective means to examine the binding mode of the NHC without the need for isotope labeling; it instead uses the chemical shift of the N(1s) signal.^[11] Besides the observed N(1s) signal of C₁₁-IMe@UCNPs, a subtle shift towards higher binding energies compared to the NHC salt is observed (see the Supporting Information). The NHC salt showed a binding energy of 401.2 eV and that of the NHC to the UCNP 401.7 eV, with a standard deviation of 0.1 eV. The higher binding energy can be explained by the coordination of the NHC to the strong Lewis acid Y^{III}, which withdraws a substantial amount of electron density from the NHC and, therefore, from the nitrogen atom. Consequently, relative to the NHC salt, more energy is required to remove an electron from the N(1s)

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orbital, which results in a slight shift towards higher binding energies. As the Y(1s) signal overlaps with the N(1s) signal in the XPS analysis, no conclusion can be drawn as to whether the Y(1s) signal is shifted by the binding of the NHC or not. The related Y(3d) signal could not be observed.

The C₁₁-IMe@UCNPs stability was investigated by reanalyzing a representative sample after storage for five months at room temperature in solution. It was found to be unchanged, which illustrates a remarkable long-term stability. Furthermore, knowing that the standard OA@UCNPs are unstable at pH 4 or lower due to protonation of the OA,^[15a] the NMR dispersion was acidified to pH3 and 2 and measured again after more than 6 h. No change in the shift of the carbon atom resonance could be observed, and the dispersion remained stable. Acidifying the dispersion to pH 1, however, led to the removal of the NHC ligand from the particles, as visualized by the dispersion becoming yellow in color. NMR spectroscopy revealed a new signal about 30 ppm lower than the carbene signal, which is likely to be attributed to C₁₁-IMe-HCl (see the Supporting Information). These results indicate that the C11-IMe@UCNPs possess superior stability to the OA@UCNPs under acidic conditions, which could be advantageous for certain applications. Treating the $C_{11}\mbox{-}IMe@UCNPs$ with an excess of tetraethyleneglycol monomethyl ether phosphate led to the exchange of C₁₁-IMe, and after workup the UCNPs could be obtained from the aqueous phase. It is likely that the tremendous excess of the added ligand enforces an exchange, through a dynamic equilibrium, which is unrelated to the binding strength of the NHC. Previous studies showed that thiols are able to remove NHCs from a NP surface, although the covalent bond of the NHC is stronger than the metal-sulfur bond.^[4e,11]

With the NHC binding to the UCNP, the possibility of changes in size and shape as a result of leaching during the ligand-exchange reaction were elucidated by TEM analysis for the same sample batch that was analyzed by TGA. The particle size and shape remained the same; a bimodal size distribution was obtained $(9.0 \pm 0.9 \text{ nm}, 20.0 \pm 1.2 \text{ nm})$, which can likely be attributed to the manually controlled heating rate during the synthesis leading to heterogeneous nucleation sites (Figure 3).

Having the C_{11} -IMe@UCNPs in hand it was of interest to determine if they are capable of inducing photoreactions, such as an isomerization of the *trans* to the *cis* form of an azobenzene, which is a prime example of a photoswitchable molecule. These photoswitches are of particular interest in the



Figure 3. TEM analysis of OA@UCNPs and C_{11} -IMe@UCNPs. A bimodal size distribution was obtained in both cases.

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field of host-guest interactions and the controlled formation or release of inclusion complexes.^[1g,h,19b] Therefore, a 20 μ m sample of Azo-TEG (Figure 4) in toluene containing a stable 2 μ m dispersion of C₁₁-IMe@UCNPs was irradiated for 21 h with a defocused NIR laser ($\lambda = 980$ nm,



Figure 4. C₁₁-IMe@UCNP-induced isomerization of an azobenzene photoswitch (A_1 , A_2) and cleavage of an *ortho*-nitrobenzyl ester (B_1 , B_2) in toluene. The image (**C**) shows visualization of the NIR laser beam as a result of the upconversion process.

 0.22 W cm^{-2}). To the best of our knowledge, this is one of the lowest reported intensities for UCNP-induced transformations.^[19] The isomerization from *trans* to *cis* is visualized by the clear decrease in the absorption band, and even approaches the photostationary state of the azobenzene. Under the same conditions it was possible to cleave an *ortho*-nitrobenzyl ester, an important example of a photocleavable group, in 22 h. Such photocleavable groups are readily employed for the controlled light-induced release of drugs.^[20]

The switching process was accelerated by a factor of approximately 3 within a timeframe of 2 h when the azobenzene photoswitch was bound to the NHC ligand (Figure 5, for the corresponding UV/Vis spectra see the



Figure 5. Azo-NHC@UCNP-induced isomerization of the immobilized azobenzene in toluene. Accelerated photoisomerization through the enforced proximity of the azobenzene to the UCNP surface compared to C₁₁-IMe@UCNPs and Azo-TEG. Both isomerizations were induced by an NIR laser ($\lambda = 980$ nm, 0.22 W cm⁻²).

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Supporting Information). The alkyne-functionalized azobenzene was connected to an azide moiety in the backbone of the NHC through a click reaction. This example illustrates how NHCs can bring functionality very close to a NP surface. The accelerated photoisomerization of the immobilized azobenzene is attributed to the closer and permanent proximity to the surface.

In conclusion, for the first time we have introduced NHCs as ligands for the stabilization of high oxidation state metal NPs. The NHC-stabilized UCNPs are obtained in a simple ligand-exchange reaction from the standard OA@UCNPs, are superior in stability under acidic conditions, and show general and high long-term stability. In addition, the new NHC@UCNPs were successfully applied in NIR-induced photoreactions.

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Conflict of interest

The authors declare no conflict of interest.

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- Selected examples for applications of nanoparticles: a) C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, Chem. Rev. 2005, 105, 1025; b) D. Astruc, F. Lu, J. R. Aranzaes, Angew. Chem. Int. Ed. 2005, 44, 7852; Angew. Chem. 2005, 117, 8062; c) R. J. White, R. Luque, V. L. Budarin, J. H. Clark, D. J. Macquarrie, Chem. Soc. Rev. 2009, 38, 481; d) L. D. Pachón, G. Rothenberg, Appl. Organomet. Chem. 2008, 22, 288; e) R. V. Jagadeeshm, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, Science 2013, 342, 1073; f) J. H. Schenkel, A. Samanta, B. J. Ravoo, Adv. Mater. 2014, 26, 1076; g) A. Samanta, B. J. Ravoo, Angew. Chem. Int. Ed. 2014, 53, 12946; Angew. Chem. 2014, 126, 13160; h) G. Y. Tonga, Y. Jeong, B. Duncan, T. Mizuhara, R. Mout, R. Das, S. T. Kim, Y.-C. Yeh, B. Yan, S. Hou, V. M. Rotello, Nat. Chem. 2015, 7, 597.
- [2] a) B. L. Cushing, V. L. Kolesnichenko, C. J. O'Connor, *Chem. Rev.* 2004, 104, 3893; b) L. S. Ott, R. G. Finke, *Coord. Chem. Rev.* 2007, 251, 1075.
- [3] Selected Reviews on NHCs: a) F. E. Hahn, M. C. Jahnke, Angew. Chem. Int. Ed. 2008, 47, 3122; Angew. Chem. 2008, 120, 3166; c) S. Díez-González, N. Marion, S. P. Nolan, Chem. Rev. 2009, 109, 3612; d) T. Dröge, F. Glorius, Angew. Chem. Int. Ed. 2010, 49, 6940; Angew. Chem. 2010, 122, 7094; e) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, Nature 2014,

510, 485; f) A. V. Zhukhovitskiy, M. J. MacLeod, J. A. Johnson, *Chem. Rev.* **2015**, *115*, 11503.

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- [4] Selected examples for NHCs as ligands for unsupported nanoparticles: a) J. Vignolle, T. D. Tilley, Chem. Commun. 2009, 7230; b) E. C. Hurst, K. Wilson, I. J. S. Fairlamb, V. Chechik, New J. Chem. 2009, 33, 1837; c) P. Lara, O. Rivada-Wheelaghan, S. Conejero, R. Poteau, K. Philippot, B. Chaudret, Angew. Chem. Int. Ed. 2011, 50, 12080; Angew. Chem. 2011, 123, 12286; d) D. Gonzalez-Galvez, P. Lara, O. Rivada-Wheelaghan, S. Conejero, B. Chaudret, K. Philippot, P. W. N. M. van Leeuwen, Catal. Sci. Technol. 2013, 3, 99; e) X. Ling, N. Schaeffer, S. Roland, M.-P. Pileni, Langmuir 2013, 29, 12647; f) E. A. Baquero, S. Tricard, J. C. Flores, E. de Jesús, B. Chaudret, Angew. Chem. Int. Ed. 2014, 53, 13220; Angew. Chem. 2014, 126, 13436; g) H.-X. Liu, X. He, L. Zhao, Chem. Commun. 2014, 50, 971; h) M. Rodríguez-Castillo, D. Laurencin, F. Tielens, A. van der Lee, S. Clément, Y. Guari, S. Richeter, Dalton Trans. 2014, 43, 5978; i) S. G. Song, C. Satheeshkumar, J. Park, J. Ahn, T. Premkumar, Y. Lee, C. Song, Macromolecules 2014, 47, 6566.
- [5] Selected examples for NHCs as ligands for supported nanoparticles: a) K. V. S. Ranganath, J. Kloesges, A. H. Schäfer, F. Glorius, Angew. Chem. Int. Ed. 2010, 49, 7786; Angew. Chem. 2010, 122, 7952; b) D. Yu, M. X. Tan, Y. Zhang, Adv. Synth. Catal. 2012, 354, 969; c) J. B. Ernst, S. Muratsugu, F. Wang, M. Tada, F. Glorius, J. Am. Chem. Soc. 2016, 138, 10718.
- [6] Selected examples for NHCs on metal surfaces: a) A. V. Zhukhovitskiy, M. G. Mavros, T. V. Voorhis, J. A. Johnson, J. Am. Chem. Soc. 2013, 135, 7418; b) C. M. Crudden, J. H. Horton, I. I. Ebralidze, O. V. Zenkina, A. B. McLean, B. Drevniok, Z. She, H.-B. Kraatz, N. J. Mosey, T. Seki, E. C. Keske, J. D. Leake, A. Rousina-Webb, G. Wu, Nat. Chem. 2014, 6, 409; c) G. Wang, A. Rühling, S. Amirjalayer, M. Knor, J. B. Ernst, C. Richter, H.-J. Gao, A. Timmer, H.-Y. Gao, N. L. Doltsinis, F. Glorius, H. Fuchs, Nat. Chem. 2017, 9, 152.
- [7] C. Richter, K. Schaepe, F. Glorius, B. J. Ravoo, *Chem. Commun.* 2014, 50, 3204.
- [8] a) L. S. Ott, M. L. Cline, M. Deetlefs, K. R. Seddon, R. G. Finke, J. Am. Chem. Soc. 2005, 127, 5758; b) L. S. Ott, S. Campbell, K. R. Seddon, R. G. Finke, Inorg. Chem. 2007, 46, 10335; c) J. D. Scholten, G. Ebeling, J. Dupont, Dalton Trans. 2007, 5554; d) J. D. Scholten, J. Dupont, Organometallics 2008, 27, 4439; e) Y. E. Corilo, F. M. Nachtigall, P. V. Abdelnur, G. Ebeling, J. Dupont, M. N. Eberlin, RSC Adv. 2011, 1, 73.
- [9] A. Ferry, K. Schaepe, P. Tegeder, C. Richter, K. M. Chepiga, B. J. Ravoo, F. Glorius, ACS Catal. 2015, 5, 5414.
- [10] M. J. MacLeod, J. A. Johnson, J. Am. Chem. Soc. 2015, 137, 7974.
- [11] A. Rühling, K. Schaepe, L. Rakers, B. Vonhören, P. Tegeder, B. J. Ravoo, F. Glorius, *Angew. Chem. Int. Ed.* **2016**, *55*, 5856; *Angew. Chem.* **2016**, *128*, 5950.
- [12] NHCs have been used to stabilize nanoclusters by binding to oxidized metal centers: a) J. L. Durham, W. B. Wilson, D. N. Huh, R. McDonald, L. F. Szczepura, *Chem. Commun.* 2015, 51, 10536; NHC derivatives have been applied in stabilizing MgO nanoparticles: b) M. Shaikh, M. Sahu, S. Khilari, A. K. Kumar, P. Maji, K. V. S. Ranganath, *RSC Adv.* 2016, 6, 82591; c) M. Shaikh, M. Sahu, P. K. Gavel, G. R. Turpu, S. Khilari, D. Pradhan, K. V. S. Ranganath, *Catal. Commun.* 2016, 84, 89.
- [13] P. Rahman, M. Green, Nanoscale 2009, 1, 214.
- [14] a) G. Chen, H. Qiu, P. N. Prasad, X. Chen, *Chem. Rev.* 2014, *114*, 5161; b) J. Zhou, Q. Liu, W. Feng, Y. Sun, F. Li, *Chem. Rev.* 2015, *115*, 395; c) H. Dong, S.-R. Du, X.-Y. Zheng, G.-M. Lyu, L.-D. Sun, L.-D. Li, P.-Z. Zhang, C. Zhang, C.-H. Yan, *Chem. Rev.* 2015, *115*, 10725.
- [15] Selected examples on different applications of upconversion nanoparticles: a) N. Bogdan, F. Vetrone, G. A. Ozin, J. A. Capobianco, *Nano Lett.* **2011**, *11*, 835; b) B. F. Zhang, M. Frigoli, F. Angiuli, F. Vetrone, J. A. Capobianco, *Chem. Commun.* **2012**,

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48, 7244; c) Q. Yu, E. M. Rodriguez, R. Naccache, P. Forgione,
G. Lamoueux, F. Sanz-Rodriguez, D. Scheglmann, J. A. Capobianco, *Chem. Commun.* 2014, 50, 12150; d) J. Lai, Y. Zhang, N. Pasquale, K.-B. Lee, *Angew. Chem. Int. Ed.* 2014, 53, 14419; *Angew. Chem.* 2014, 126, 14647; e) W. Li, Z. Chen, L. Zhou, Z. Li, J. Ren, X. Qu, J. Am. Chem. Soc. 2015, 137, 8199; f) T. Wu,
N. R. Branda, *Chem. Commun.* 2016, 52, 8636; g) G. Jalani, R. Naccache, D. H. Rosenzweig, L. Haglund, F. Vetrone, M. Cerruti, J. Am. Chem. Soc. 2016, 138, 1078.

- [16] J.-C. Boyer, F. Vetrone, L. A. Cuccia, J. A. Capobianco, J. Am. Chem. Soc. 2006, 128, 7444.
- [17] P. L. Arnold, I. J. Casely, Chem. Rev. 2009, 109, 3599.
- [18] H. Liu, C. T. Xu, G. Dumlupinar, O. B. Jensen, P. E. Andersen, S. Andersson-Engels, *Nanoscale* 2013, 5, 10034.

- [19] a) Z. Chen, W. Sun, H.-J. Butt, S. Wu, *Chem. Eur. J.* 2015, 21, 9165; b) N. Möller, T. Hellwig, L. Stricker, S. Engel, C. Fallnich, B. J. Ravoo, *Chem. Commun.* 2017, 53, 240.
- [20] a) S. V. Wegner, O. I. Sentürk, J. P. Spatz, *Sci. Rep.* 2015, *5*, 18309; b) S. Wu, H.-J. Butt, *Adv. Mater.* 2016, *28*, 1208; c) B. Yan, J.-C. Boyer, D. Habault, N. R. Branda, Y. Zhao, *J. Am. Chem. Soc.* 2012, *134*, 16558; d) Y. Yang, F. Liu, X. Liu, B. Xing, *Nanoscale* 2013, *5*, 231; e) S. Mura, J. Nicolas, P. Couvreur, *Nat. Mater.* 2013, *12*, 991; f) M. S. Kim, S. L. Diamond, *Bioorg. Med. Chem. Lett.* 2006, *16*, 4007.

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Stabilization of High Oxidation State Upconversion Nanoparticles by N-Heterocyclic Carbenes



Up, up, and carbene: High oxidation state NaYF₄:Yb,Tm upconversion nanoparticles (UCNPs) were stabilized by N-heterocyclic carbenes (NHCs) through a ligand-exchange reaction from a welldefined precursor and characterized in detail. The ligands for such nanoparticles require different properties compared to elemental metal nanoparticles. This new photoactive material was employed in reactions of photoresponsive molecules.

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