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Electronic Supplementary Information

One-Pot Synthesis of Functionalized Germanium Nanocrystals from a Single Source Precursor

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Figures

Experimental Details

Materials and Instrumentation

All reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or in an inert atmosphere glove box (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[1] manufactured by Innovative Technology, Inc., degassed (freeze-pump-thaw method) and stored under an atmosphere of nitrogen prior to use. 3-Dimethylamino-1-propyne, 1-dodecene and diphenylether were purchased from Aldrich, dried over CaH_2 and distilled under nitrogen prior to use. $Li[BH_4]$ and ^nBuLi (2.5 M solution in hexanes) were purchased from Aldrich and used as received. Ph_3PCMe_2•GeH_2•BH_3 (**1**) was prepared according to a literature procedure.[2]

FT-IR spectroscopy was performed using a Thermo Nicolet Magna 750 IR spectrometer; a toluene suspension of each sample was deposited onto a KBr plate and the solvent was allowed to evaporate to yield a thin film. Transmission electron microscopy (TEM) images were taken with a JOEL 2011TEM with LaB_6 electron gun using an accelerating voltage of 200 kV. TEM samples were prepared by depositing a droplet of dilute toluene suspension of functionalized Ge nanocrystal (GeNCs) onto a holey carbon coated copper grid and the solvent was removed under vacuum. The nanocrystal size was averaged for no fewer than 200 particles using Gatan Digital Micrograph software (Version 2.02.800.0). High-resolution (HR) TEM images were obtained from Hitachi-9500 electron microscope with an accelerating voltage of 300 kV. The HRTEM images were processed using Gatan Digital Micrograph software (Version 2.02.800.0). Photoluminescence (PL) emission and PL excitation spectra of functionalized GeNCs in 100% ethanol were taken using Carry Eclipse spectrophotometer.

Synthetic Details

Synthesis of hydrophilic GeNCs with NMe_2 surface groups:

Ph_3PCMe_2•GeH_2•BH_3 (**1**) (30 mg, 0.076 mmol) and 5 mL of 3-dimethylamino-1-propyne were transferred into a 5 mL microwave vial in a nitrogen filled glovebox. The microwave vial was sealed inside the glovebox and sonicated for 5 min before placing it into a Biotage Initiator microwave reactor. The mixture was irradiated for 2 hours at 190 °C to give a dark red solution. The volatiles were removed from the resulting mixture using a rotary evaporator and the crude product was redispersed in 8 mL of toluene with sonication, followed by addition of *ca.* 30 mL of hexane. This mixture was centrifuged at 14000 rpm to afford a red solid that was separated from the supernatant and isolated. The resulting pellet was redispersed in 40 mL of toluene/hexanes (1:4) with sonication. The cloudy mixture was centrifuged at 14000 rpm to yield a red solid and the procedure was repeated two more times to afford the GeNCs as a red solid. The hydrophilic NCs are soluble in protic solvent such as alcohols as well as aprotic solvents such as DMSO, DMF, and THF. They are also soluble in aqueous alcohol. Yield: 7 mg.

Preparation of dodecyl-capped GeNCs via microwave irradiation:

Ph_3PCMe_2•GeH_2•BH_3 (**1**) (30 mg, 0.076 mmol), 2.5 mL of 1-dodecene and 2.5 mL of diphenylether were transferred into a 5 mL microwave vial in a nitrogen filled glove box. The microwave vial was sealed inside the glovebox and sonicated for 5 min. before placing it into a Biotage Initiator microwave reactor. The reaction mixture was irradiated for 1 h at predetermined temperatures (*i.e.*, 100, 150, 190, and 250°C). A mixture of toluene/methanol (1:4; 40 mL) was added to the mixture followed by centrifugation at 14000 rpm to provide a red solid. The supernatant was decanted and discarded. The pellet was redispersed in 40 mL of toluene/methanol (1:4) mixture with sonication. The cloudy mixture was centrifuged at 14000 rpm to yield a red solid and the procedure was repeated two more times to afford the GeNCs as a red solid. Hydrophobic GeNCs were soluble in hydrophobic solvents such as toluene, $CHCl_3$, and THF. Yield: 9.5 mg for 190 °C. Lower concentrations (*i.e.*, 10 and 20 mg/5 mL) of **1** in 1:1 (v:v) 1-dodecene/diphenylether were used to produce various sizes dodecyl-GeNCs.

Synthesis of dodecyl-capped GeNCs via hot-injection method:

Ph_3PCMe_2•GeH_2•BH_3 (**1**) (60 mg, 0.16 mmol) in 1.5 mL diphenylether was injected into a hot stirring solvent mixture of 1-dodecene (5 mL) and diphenylether (4mL) at 100, 150, and 190°C under an argon atmosphere. The reaction mixture turned from colorless to yellow with the formation of a gas. After heating for 1 hour the reaction mixture turned to light yellow (100°C), yellow (150°C), and red (190°C). The reactions were quenched upon addition of 10 mL dry cold toluene. Subsequently, 40 mL of toluene/methanol (1:4) was added, followed by centrifugation at 14000 rpm to provide a yellow (for 100 and 150°C) or red (for 190°C) solid. The supernatant was decanted and discarded. The pellet was redispersed in 40 mL of toluene/methanol (1:4) with sonication. The cloudy mixture was centrifuged at 14000 rpm to yield a red solid and the procedure was repeated two more times to afford the GeNCs as a red solid. Yield: 15.2 mg at 190 °C. Reactions at 100 and 150 °C yielded trace quantities of GeNCs.

Characterization Details

Photoluminescence (PL) Lifetimes: Nanosecond (ns) lifetime measurements were performed using an excitation pulse of a 400-nm second harmonic signal from a BBO crystal pumped by 800-nm pulses from a Ti:Sapphire laser (Coherent RegA900 with 65 fs pulse width and 250 kHz repetition rate) with average excitation power of 5.28 mW. Time-resolved PL was recorded using a time-correlated single-photon-counting (TCSPC) unit (Picoharp 300, Picoquant) equipped with a single-photon avalanche photodiode (SPAD, PDM Series by Micro Photon Devices) and coupled to a monochromator (Acton SP2500, Princeton Instruments). The TCSPC system has a time resolution of 50 ± 4 ps. A 435-nm long pass filter (Edmund optics) was placed at the entrance of the spectrometer to block scattered laser pulses. For microsecond carrier recombination lifetime measurements, 1 kHz frequency-doubled 400 nm pulses from another Ti:Sapphire laser (Coherent Legend Elite, 45 fs pulse width) were used to excite the PL at an average excitation power of 4.8 mW, however, no microsecond PL component was observed A fast silicon photodiode (Thorlabs, PDA36A, rise time 20.6 ns) coupled to a 300 MHz oscilloscope (Tektronix) was used to measure the microsecond carrier recombination lifetime. The photodiode was placed at a path perpendicular to the excitation beam and 10-nm bandpass filters (Edmund Optics) were used to select a particular emission wavelength. The carrier recombination lifetimes were accurately fitted by double exponential decay:

$$y(t) = Ae^{-t/\tau_1} + Be^{-t/\tau_2} + y_0 \qquad [1]$$

where τ_1 and τ_2 are the decay times and A and B are the respective amplitudes of the decay components. The constant offset term, y_0 was insignificant compared to the coefficients A and B.

XPS: X-ray photoelectron spectroscopy (XPS) analyses were performed using a Kratos Axis Ultra instrument operating in energy spectrum mode at 210 W. Samples were prepared by depositing a solution of functionalized GeNCs onto a copper foil substrate as films. The base and operating chamber pressure were maintained at 10^{-7} Pa. A monochromatic Al Kα source (λ = 8.34 Å) was used to irradiate the samples, and the spectra were obtained with an electron take-off angle of 90°. To minimize sample charging, the charge neutralizer filament was used when required. Survey spectra were collected using an elliptical spot with major and minor axis lengths of 2 and 1 mm, respectively, and 160 eV pass energy with a step of 0.33 eV. CasaXPS software (VAMAS) was used to interpret high-resolution spectra. All spectra were internally calibrated to the C 1s emission (284.8 eV). After calibration, a Shirley-type background was applied to remove most of the extrinsic loss structure. The FWHM for all the fitted peaks was maintained below 1.2 eV.

Quantum yield (QY) determination:

Background subtracted UV-vis absorption spectra and solvent corrected PL emission spectra of predefined dilutions of NMe_2-GeNCs solution (in ethanol) and standard (in cyclohexane) were collected at excitation wavelength 350 nm. The integrated intensities (from 360 – 600 nm) were determined from the solvent corrected PL spectra and plotted vs. respective absorbance at 350 nm. QY was determined using the relationship noted below; where $\mathrm{Slope}_{\mathrm{GeNCs}}$ and $\mathrm{Slope}_{\mathrm{Std}}$ were determined from the plot in **Fig. S10** and n is refractive index of the solvent.[3] The PL standard of choice for the present study was 9,10-diphenylanthracene (QY = 97%).[4]

QY of NMe_2-GeNCs,

$$\Phi_{GeNCs} = \Phi_{Std} \frac{Slope_{GeNCs}}{Slope_{Std}} \left(\frac{n_{ethanol}}{n_{cyclohexane}} \right)^2$$

$= 0.97\times(1144.04/55173.46)\times(1.361/1.4266)^{\wedge 2}$

$= 0.018 = 1.8\%$

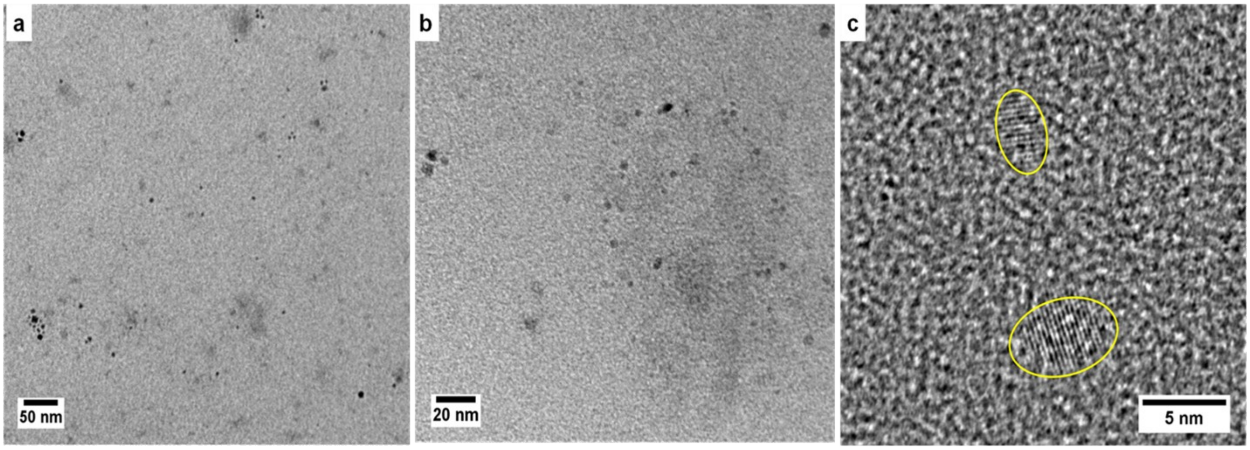


Fig. S1. Representative brightfield TEM and HRTEM images of dodecyl-GeNCs obtained from MI decomposition of **1** at 30 mg/ 5mL at 150^{o}C in 1:1 (v:v) dodecene/diphenylether.

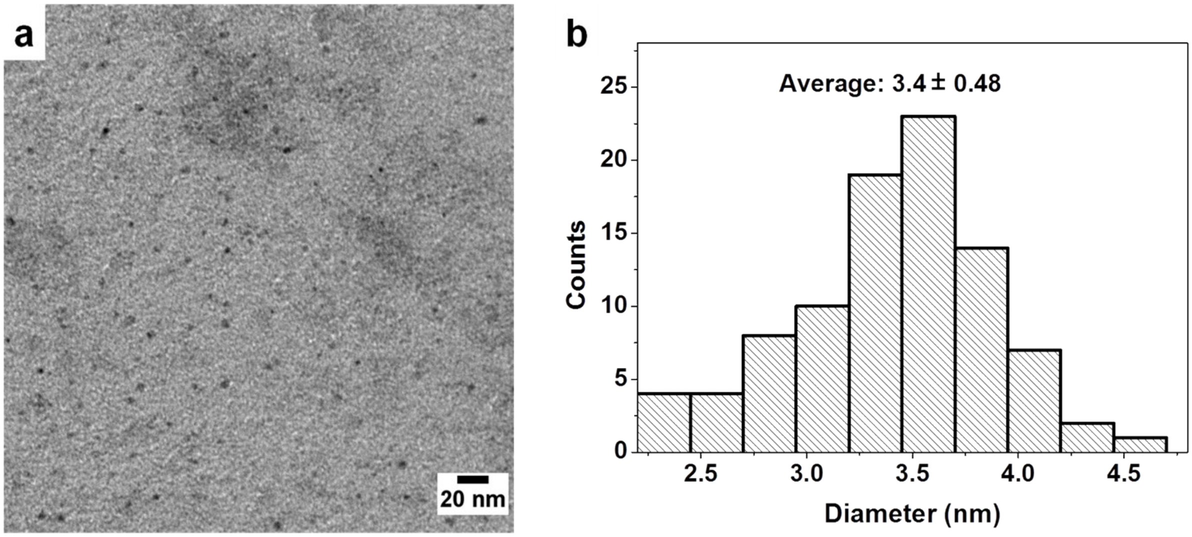


Fig. S2. Representative brightfield TEM image and size-distribution of dodecyl-GeNCs obtained from MI decomposition of **1** at 10 mg/ 5mL at 190^{o}C in 1:1 (v:v) dodecene/diphenylether.

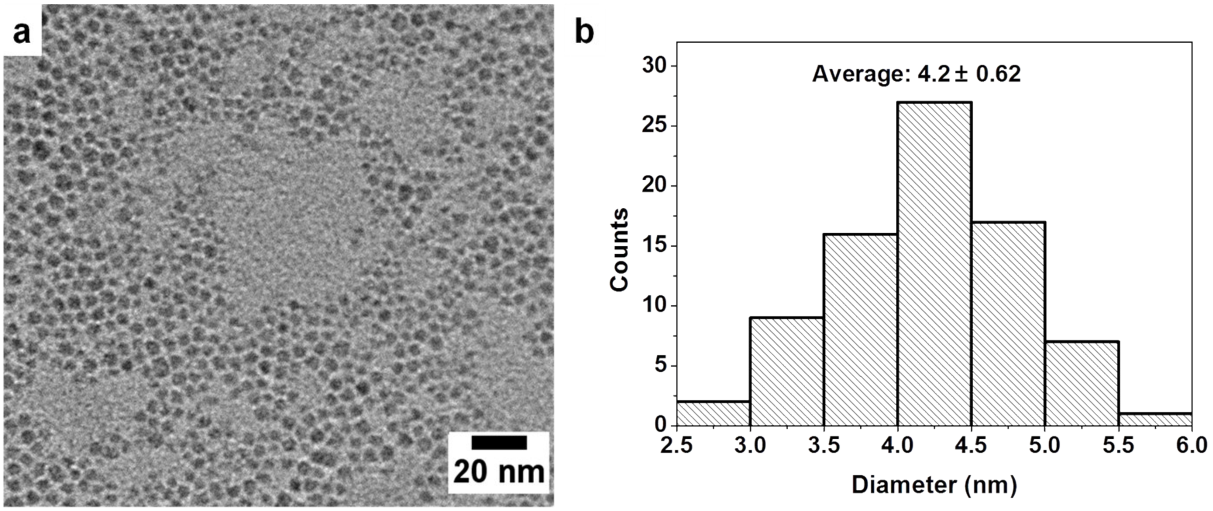


Fig. S3. Representative brightfield TEM image and size-distribution of dodecyl-GeNCs obtained from MI decomposition of **1** at 20 mg/5 mL at 190^{o}C in 1:1 (v:v) dodecene/diphenylether.

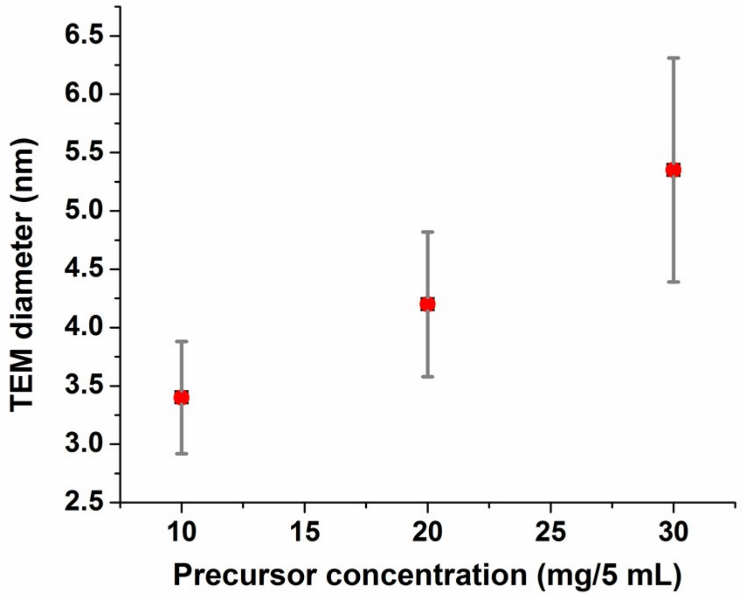


Fig. S4. The relationship between TEM determined particle diameter and precursor **1** concentration for reactions performed at 190^{o}C in 1:1 (v:v) dodecene/diphenylether.

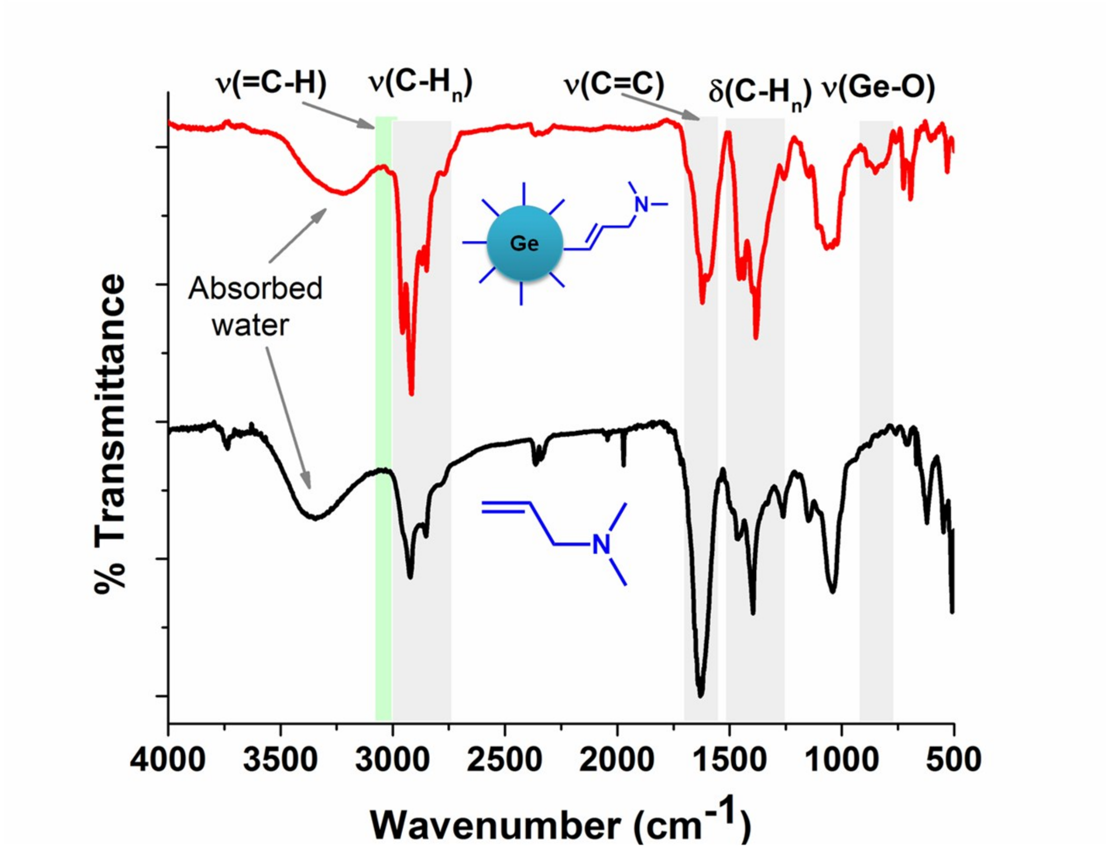


Fig. S5. FTIR spectra of NMe$_2$-GeNCs (Top) and neat 3-dimethylamino-1-propene (Bottom).

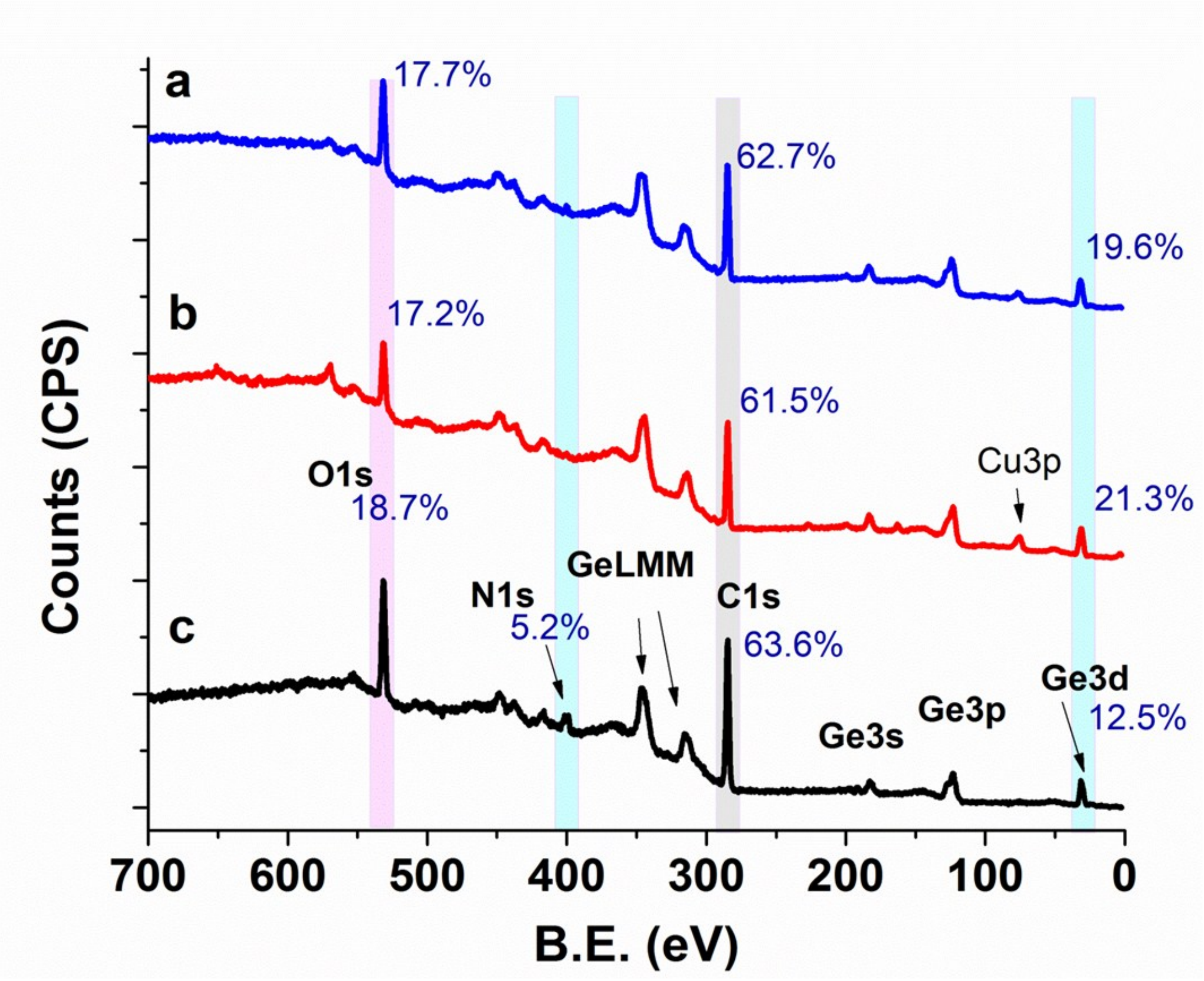


Fig. S6 Survey XP spectra of: (a) Dodecyl-GeNCs prepared by HI (190°C) induced decomposition of **1** at 30 mg/mL in 1:1 (v:v) dodecene/diphenylether. (b) Dodecyl-GeNCs and (c) Me_2N-GeNCs synthesized by MI (190°C) induced decomposition of **1** at 30 mg/ 5 mL in 1:1 (v:v) dodecene/diphenylether.

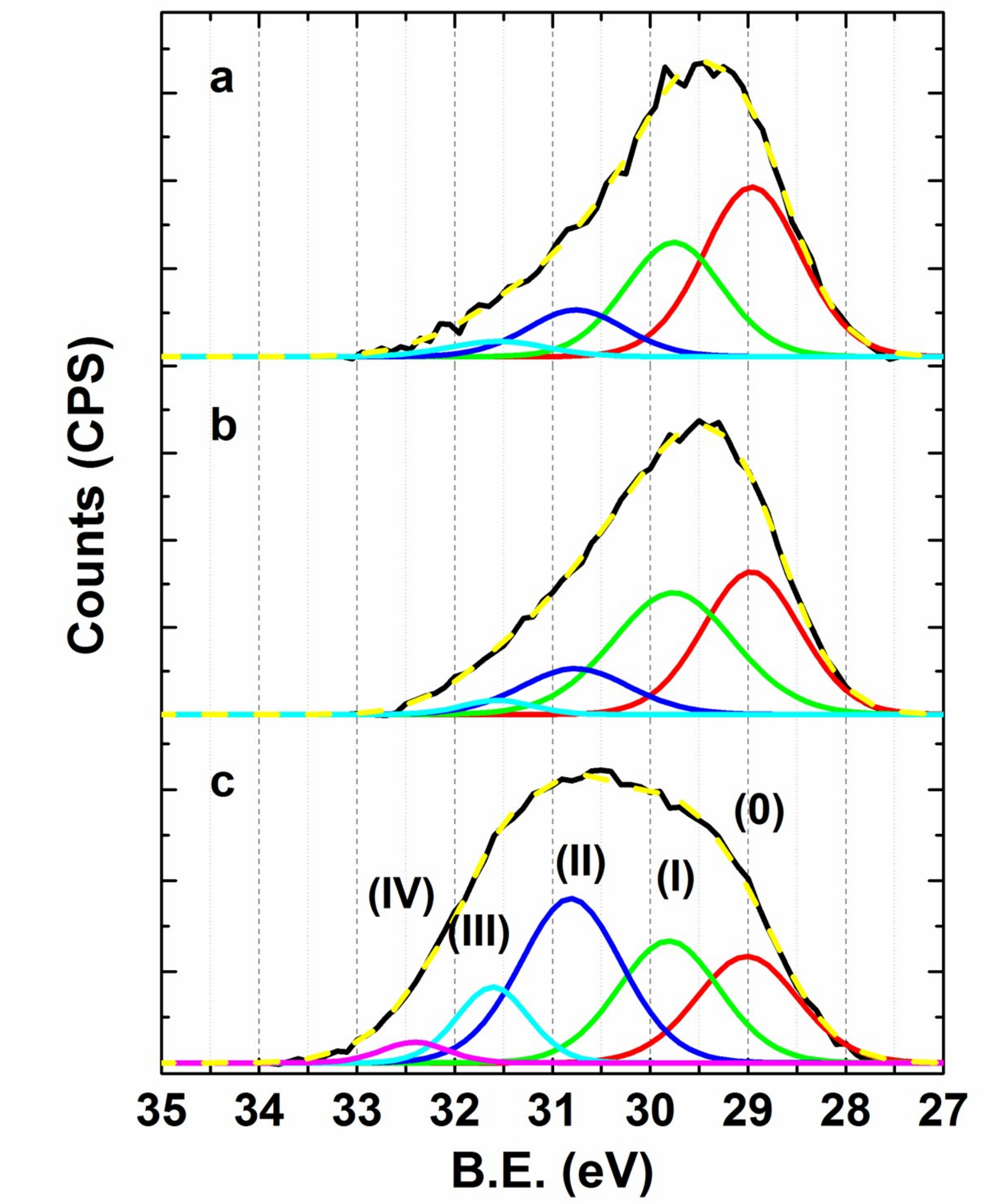
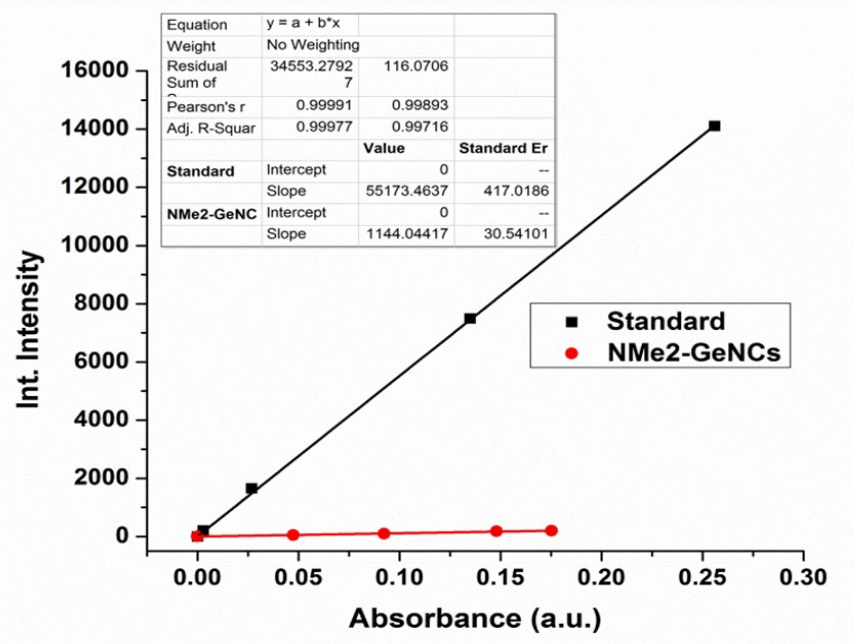


Fig. S7 High-resolution XP spectra of the Ge 3d spectral region for dodecyl-GeNCs synthesized by MI induced decomposition of **1** at precursor concentrations of: (a) 10, (b) 20, and (c) 30 mg/ 5mL in 1:1 (v:v) dodecene/diphenylether.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of	34553.27927	116.0706	
Pearson's r	0.99991	0.99893	
Adj. R-Squar	0.99977	0.99716	
		Value	**Standard Er**
Standard	Intercept	0	--
	Slope	55173.4637	417.0186
NMe2-GeNC	Intercept	0	--
	Slope	1144.04417	30.54101

Fig. S8. PL quantum yield determination for Me_2N-GeNCs.

References

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(2) A. K. Swarnakar, S. M. McDonald, K. C. Deutsch, P. Choi, M. J. Ferguson, R. McDonald, and E. Rivard, *Inorg. Chem.* 2014, **53**, 8662.

(3) A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067.

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