Supporting Information for

Soft-Template Synthesis of Nitrogen-doped Carbon Nanodots: Tunable Visible-light Photoluminescence and Phosphor-based Light-Emitting Diodes

Sungan Do[†], Woosung Kwon[†] and Shi-Woo Rhee*

Department of Chemical Engineering,

Pohang University of Science & Technology (POSTECH),

77 Cheongam-ro, Nam-gu, Pohang 790-784, Republic of Korea.

E-mail: srhee@postech.ac.kr; Tel: +82-54-279-2265; Fax: 82-54-279-8619

[†]These authors equally contributed to this work.

*To whom correspondence should be addressed. E-mail: srhee@postech.ac.kr

a. Experimental details

Synthesis of N-doped carbon nanodots (N-CNDs).

As adding 3g of citric acid to 3mL of water (5 M), we prepared carbon source. In order to in ject nitrogen atom, ethylenediamine (EDA) was put in the carbon source with varying gram a molecule (0.7, 1.0, 1.7, 3.0, 3.3 M). After that, 1mL of oleylamine and 9mL of octadecene we re mixed to make oil phase in 3-neck round bottom flask. Putting 1mL of water solution of ca rbon and nitrogen source and 1mL of 0.5 M nitric acid in 3-neck round bottom flask, the mixt ure was vigorously stirred under argon atmosphere, thereby forming a milky emulsion. The e mulsion was heated to 250 °C for 2 h. During heating to 250 °C, emulsion solution was chan ge from opaque to transparent. As reaching 250 °C, it turned into dark brown solution. And th en resultant solution was cooled to room temperature. The resultant solution was purified wit h methanol through the method of centrifugation (3,000 rpm for 10 min). Final product was d ispersed in octane or toluene for further use.

Sample preparation.

- *Transmission electron microscopy (TEM)*. First, 1 mg of sample was dissolved in 1m L of hexane (1 mg/mL). And then, one drop of sample solution was dropped on a CF 300-Cu grid (Electron Microscopy Sciences). Finally, this sample was dried in vacuu m oven.

- *X-ray photoelectron & Ultraviolet photoelectron spectroscopy (XPS & UPS).* Above all, 10 mg of sample was dissolved in 1mL of hexane (10 mg/mL). Finally, in case of

XPS, this sample was spin coated on a silicon substrate, and for UPS, this sample was spin coated on a 50 nm Au-coated silicon substrate.

- *^{13}C nuclear magnetic resonance (NMR).* More than 100 mg of sample was dissolved i n 1 mL of chloroform-d (> 100 mg/mL), and this sample was put in a NMR sample tu be (500 MHz).

- *UV-vis absorption and photoluminescence spectroscopy (UV & PL).* First, sample is dissolved in octane. In case of UV, sample concentration is 0.2 mg/mL, and for PL is 0.05mg/mL. Finally, the sample was transferred to a 10 mm cuvette.

Characterizations.

Transmission electron microscopy (TEM) was performed using Jeol JEM-2200FS with the image Cs-corrector at an accelerating voltage of 200 kV. Infrared (IR) spectroscopy was carri ed out using a Nicolet 6700 FT-IR spectrometer. For sampling, a demountable cell (Part Num. 162-3000) with KBr windows (Pike Technologies) was used. X-ray photoelectron spectrosco py (XPS) was performed using an Escalab 250 spectrometer with an Al X-ray source (1486.6 eV). By a Bruker DRX500, ^{13}C nuclear magnetic resonance (NMR) data was measured. UV-vis absorption spectra were obtained on a Mecasys Optizen POP spectrophotometer. Photolu minescence (PL) spectra were derived by a Jasco FP-8500 fluorometer. UPS data were obtain ed by using a UHV system equipped with a VUV 5000 generator and a SES-100 detector. Its photon excitation energy was 40.8 eV (He II).

Fabrication of phosphor luminescence films

Phosphor films were made as referring to a modified version of a previously described met hod.[1] First, CNDs and N-CNDs were dissolved in toluene with 40 mg/mL concentration. And then, 5mL of this solution was mixed with a mixture of polymethyl methacrylate (MW=950,0 00, PMMA A15, Microchem) and anisole. The product was vortexed for 10 min, and left sill until the bubbles disappear. Before fabricating films, prepared 5 cm by 5 cm glass plates were cleared by detergent, water, and acetone. The glass plates were placed on a flat table and the product solution was dropped on a glass plate (2mL / 25cm^2). After overnight, the resulting p hosphor films were peeled off from glass plate.

1 W. Kwon, S. Do, J. Lee, S. Hwang, J. K. Kim, and S.-W. Rhee, *Chem. Mater.*, 2013, **25**, 18 93-1899.

b. Raman Spectroscopy

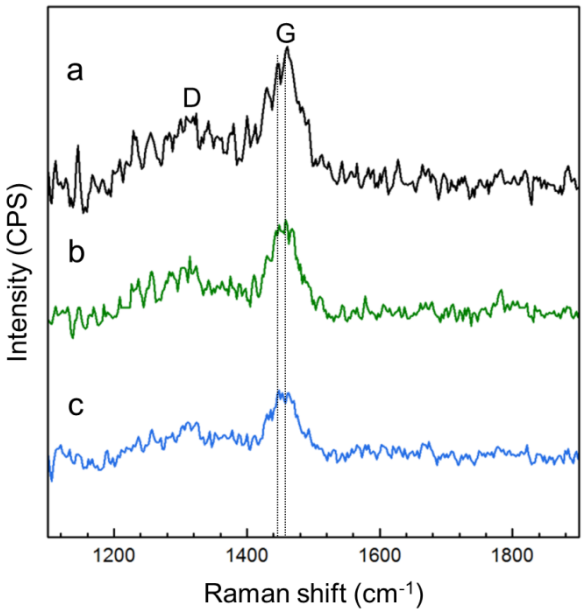


Figure S1. Raman spectroscopy of (a) **1**, (b) **2**, and (c) **3**.

NOTE: The G band (~1590 cm^{-1}) is caused by symmetric or in-plane vibration of sp^2 carbon. The G band broadens and shifts to lower wave number with disordering of sp^2 carbon.[2] In Fig ure S1, as increasing the nitrogen content, the intensity of the G band becomes gradually low er, and also, the G band position is shifted to a lower wave number from 1467 cm^{-1} to 1450 c m^{-1}.

2 J. H. Kaufman, S. Metin, D. D. Saperstein, *Phys. Rev. B*, 1989, **39**, 13053-13060.

c. ^{13}C NMR Spectroscopy

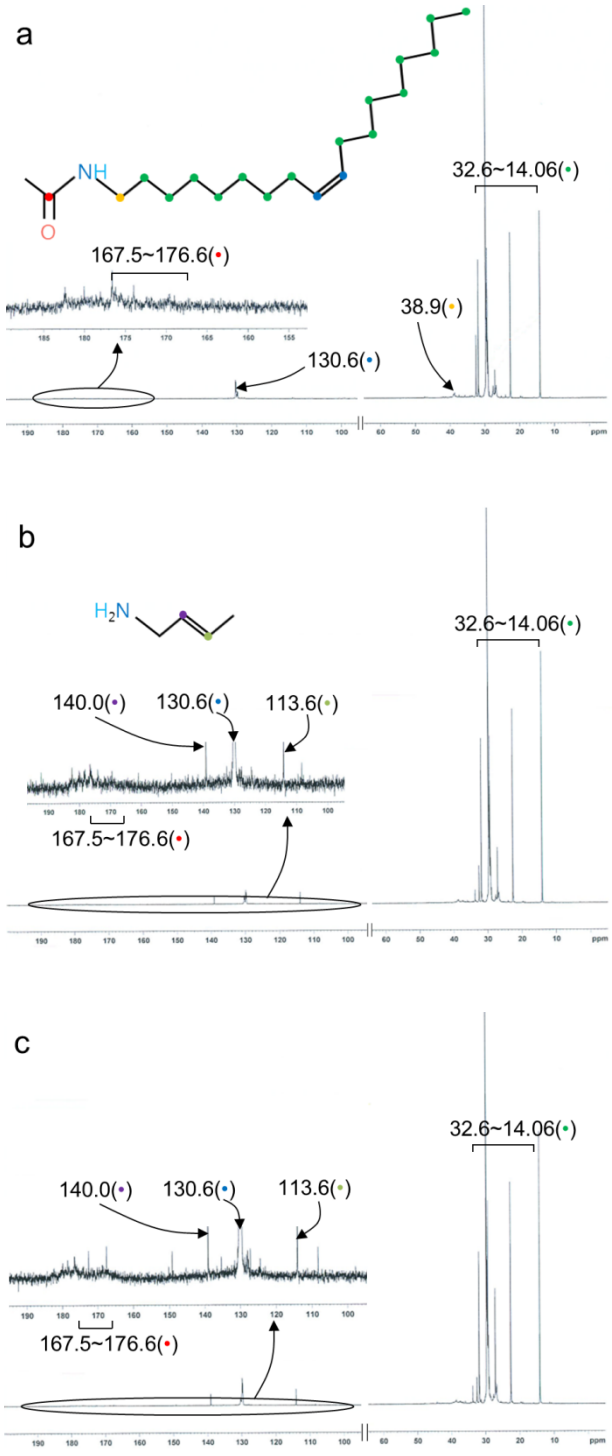


Figure S2. ^{13}C NMR spectra of (a) **1**, (b) **2**, and (c) **3** in $CDCl_3$.

NOTE: In Figure S2, The collection of peaks shown in alkyl (14.06 to 32.57 ppm), amido (38.9 ppm), acyl (167.5~176.6 ppm), and alkene (130.6 ppm) is correlated with the oleylamine, so all series of N-CND are capped by the oleylamine. In Figure S2b and S2c, however, the other s peak are appeared at 140.0 and 113.6 ppm which is related to alkene substituted with methy l amine, which indicate that as increasing the concentration of EDA, the methyl amine is mor e fabricated in the surface of N-CND.

d. XPS data

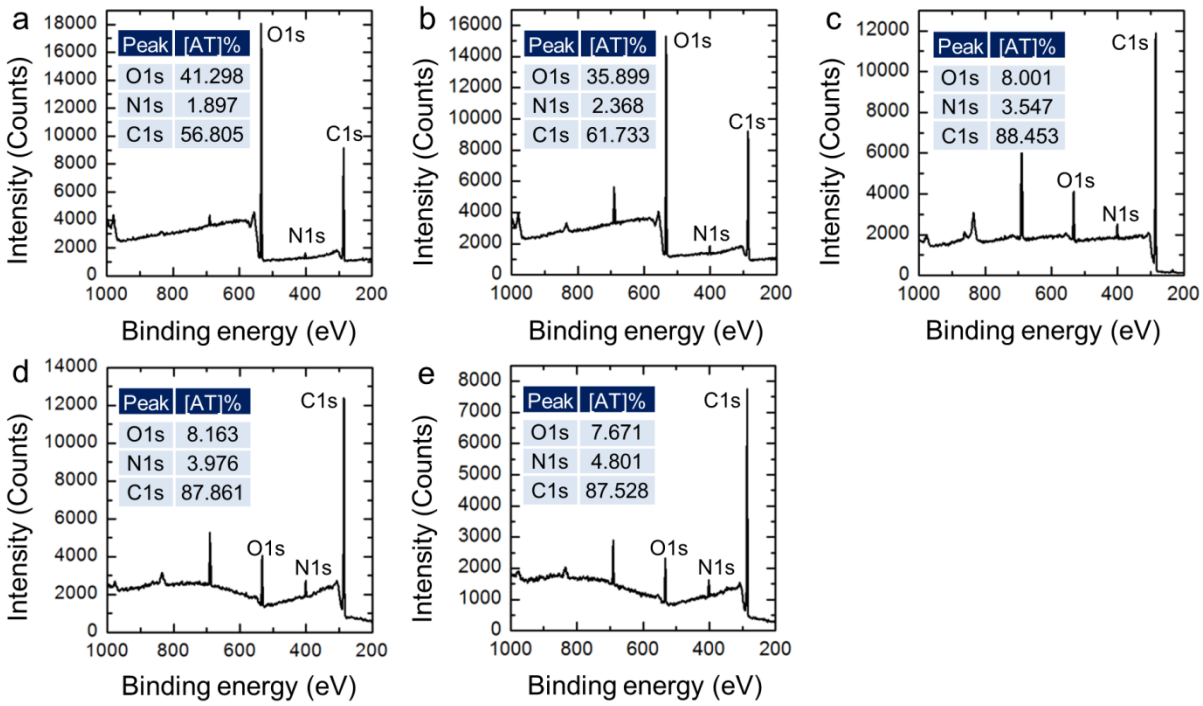


Figure S3. Full XPS data of N-CND synthesized with (a) zero, (b) 0.7, (c) 1.7, (d) 2.3 and (e) 3.0 M EDA as deposited on a silicon substrate.

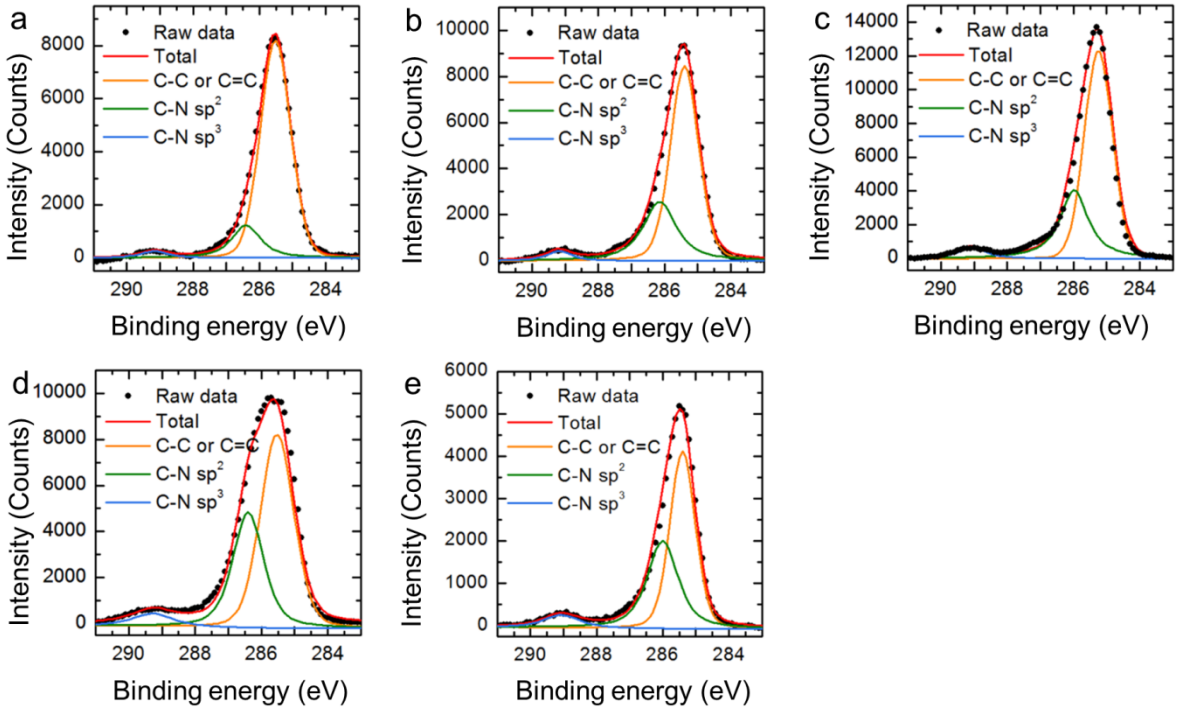


Figure S4. High-resolution XPS spectra of C1s of N-CND synthesized with (a) zero, (b) 0.7, (c) 1.7, (d) 2.3 and (e) 3.0 M EDA.

e. UV-vis absorption spectrum

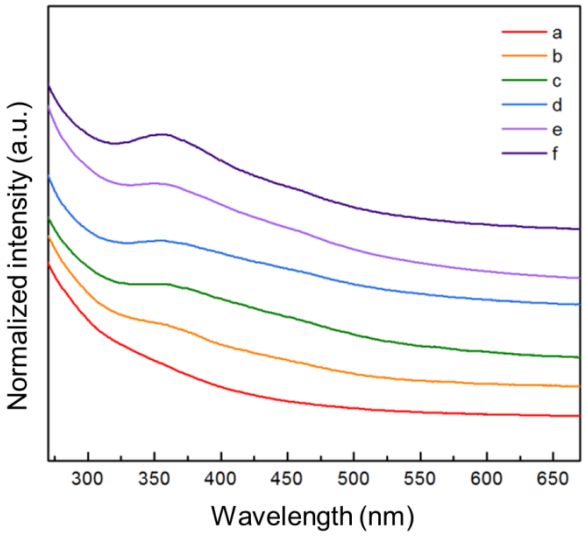


Figure S5. UV-vis absorption spectra of N-CND synthesized with (a) zero, (b) 0.7M, (c) 1.7 M, (d) 2.3M, (e) 3.0M, (f) 3.3M EDA.

f. Photographs of PL emission

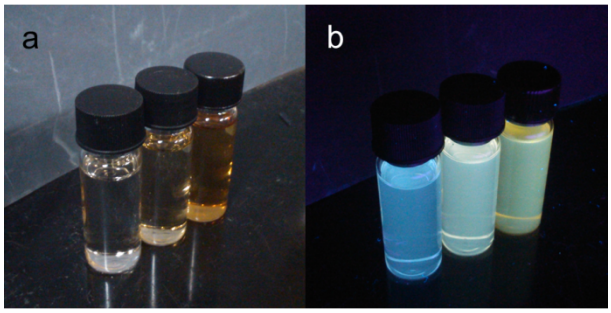


Figure S6. Photographs of PL emission at (a) day light, and (b) light whose wavelength is 360 nm. From left to right are **1**, **2**, and **3**.

g. Photoluminescence (PL) emission spectra

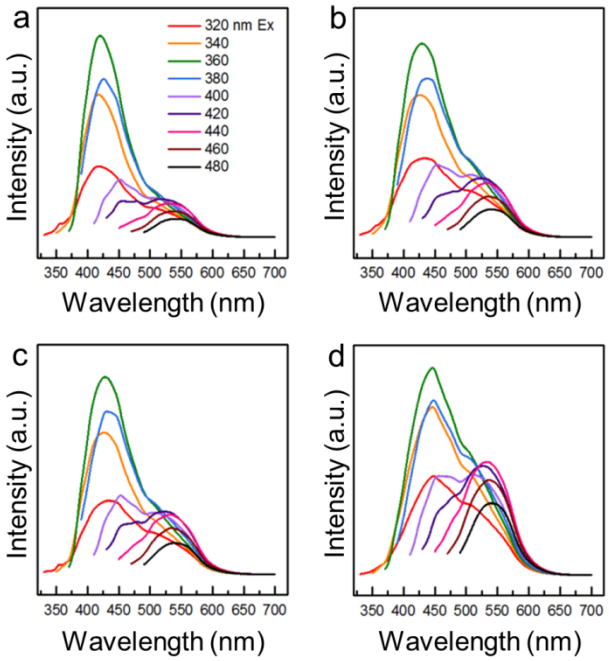
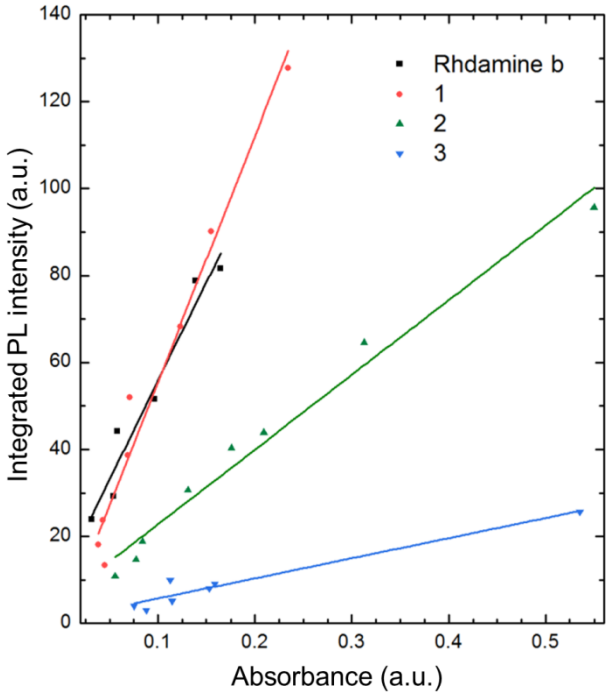


Figure S7. PL emission spectra of N-CND synthesized with (a) zero, (b) 0.7M, (c) 1.7M, and (d) 2.3M EDA.

NOTE: The surface of all N-CND is capped by oleylamine. The nitrogen in this oleylamine li gands plays a role as auxochromes, so may donate their lone pair of electrons to the antibondi ng states (or LUMOs) of the sp^2 clusters. Therefore, energy gap reduction is generated by the se ligands (Figure S7a).[3] Figures S7b-d shows that the intensity of long wavelength emission is increased with the nitrogen content, in consistence with the above mentioned reason.

3 W. Kwon, G. Lee, S. Do, T. Joo, and S.-W. Rhee, *Small.*, 2014, **10**, 506-513.

h. Quantum yield measurement



Sample	Slope	n_{std}[a]	n_x[b]	QY (%)
Rhdamine B	454.60	1.430	-	70 (lit.)
1	566.40	-	1.398	83
2	171.90	-	1.398	25
3	46.273	-	1.398	7

[a] Ethylene glycol
[b] Octane

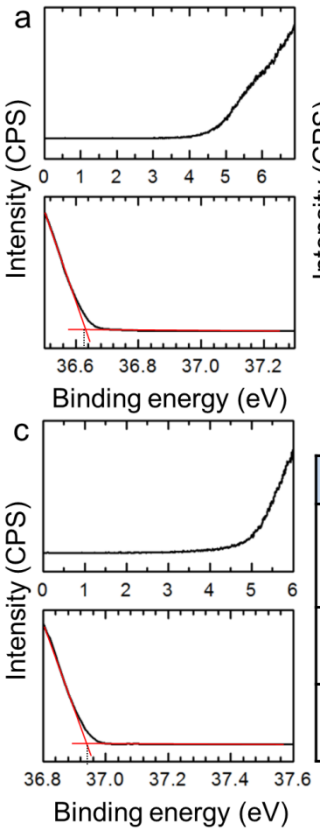
Figure S8. Integrated PL intensity versus absorbance excited at 360 nm for Rhdamine B (stan dard), **1**, **2**, and **3**. The solid lines are linear fits to the data. The parameters for calculating qua ntum yields (QYs) are in the table.

NOTE: The QY can be calculated by the following equation

$$QY_x = QY_{std}(S_x/S_s)(n_x/n_s)^2$$

where S is the slope of the fitted line, *n* is the refractive index, and the subscripts *x* and *std* de note sample and standard, respectively.

i. UPS analysis



	a	b	c
Incident photon energy (eV)	40.8	40.8	40.8
E_{cutoff} (eV)	34.53	34.74	34.84
HOMO (eV)	6.27	6.06	5.96

Figure S9. UPS data of (a) **1**, (b) **2**, and (c) **3** as deposited on an Au-coated silicon plate

NOTE: The energy gap is decided from the UPS data by the following equation: energy gap (eV) = *hv* (incident photon energy) – E_{cutoff}.

As result of calculation with this equation, energy gap of **1** is 4.17eV, that of **2** is 3.96eV, and that of **3** is 3.86eV. The increasing contents of nitrogen, the smaller energy gap is obtained.

j. Energy band structure

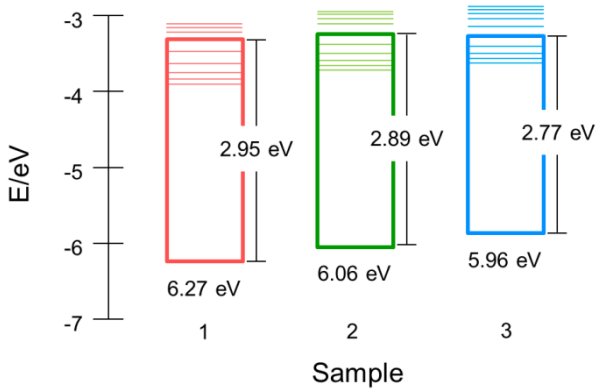


Figure S10. Energy band structure of **1**, **2**, and **3** derived from PL spectra and UPS data.

k. Stability

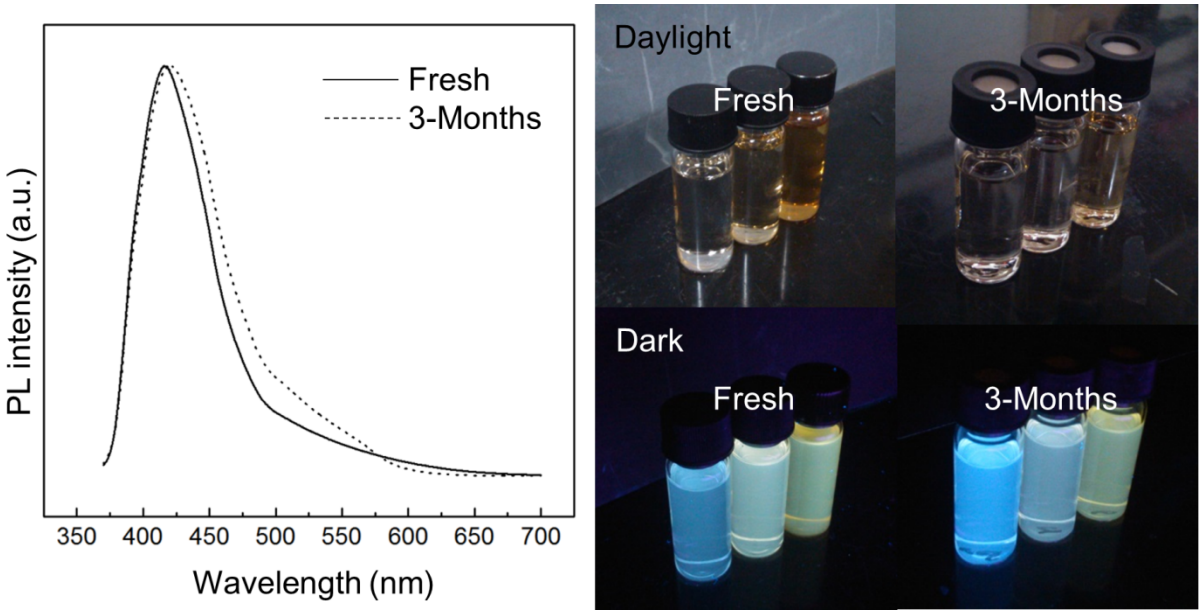


Figure S11. (Left) PL emission spectra excited at 360 nm of the fresh (dotted) and 3 months o ld (solid) **1**. (Right) Photographs of the fresh and 3 months old N-CND at day light and light whose wavelength is 360nm. From left to right are **1**, **2**, and **3**

l. Organic solubility

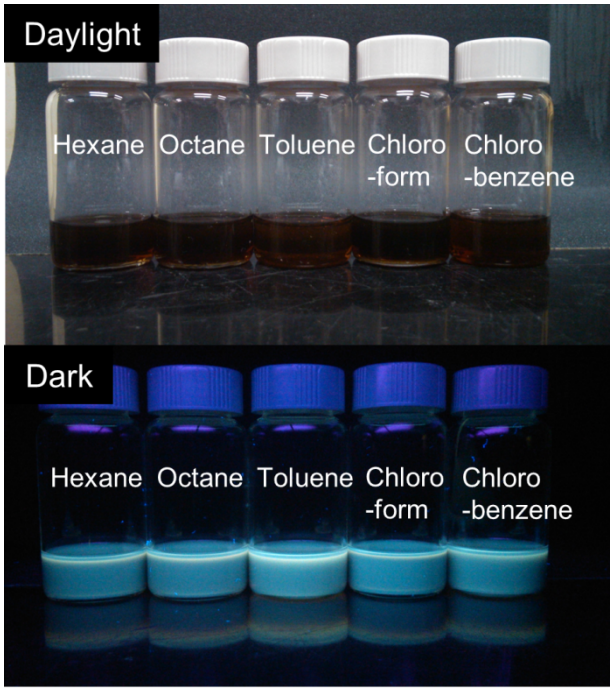
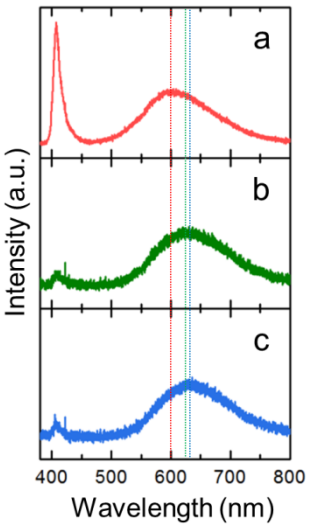
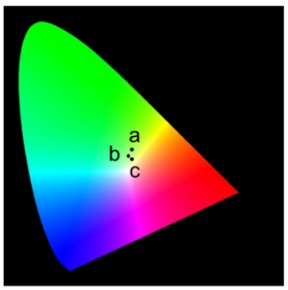


Figure S12. Photographs of N-CND solved in common solvent such as hexane, octane, toluen e, chloroform and chlorobenzene at daylight and UV light (360 nm)

m. CIE chromaticity diagram





	a	B	c
CIE x	0.3738	0.3702	0.3724
CIE y	0.4107	0.4042	0.4016
CCT (K)	4385	4440	4373

Figure S13. (Left) Emission spectra of (a) phosphor based **1** films, (b) **2** films, and (c) **3** films. (Right) CIE chromaticity coordinates and table of detail data. The CIE chromaticity diagram i s gained from http://www.picstopin.com/1280/welcome-to-freecalibrationscom/http:%7C%7Cwww*freecalibrations*com%7C_images%7CCIE1931grid%20Clean*jpg/.