Supporting Information for

Selective engineering of oxygen-containing functional groups using alkyl ligand of oleylamine for revealing luminescence mechanism of graphene oxide quantum dots

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Simulation details

Figure S1 shows the total and local density of states (DOS) of an epoxied graphene model where epoxied oxygen is surrounded single carbon hexagon domain. The red line indicates local density of epoxied oxygen atoms. Especially the small peak states between local band gap of oxygen atoms around $E_F - 0.3$ eV and $E_F + 0.87$ eV are originated from delocalized graphene carbon states by periodic cell calculation. The partial charge density plots of these states indicate that those states are delocalized graphene carbon states, not from oxygen functional groups.

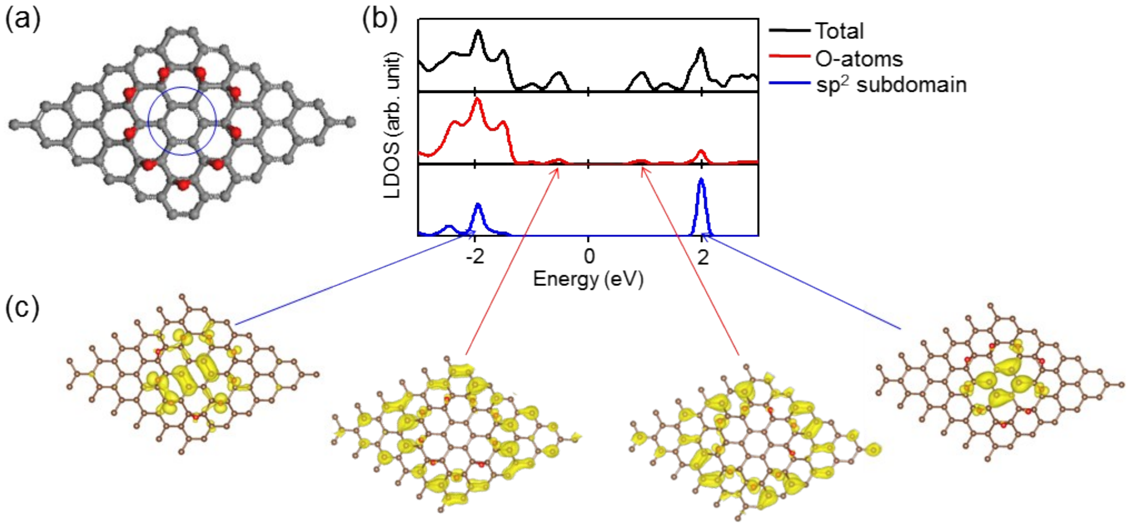

Figure S1. (a) Atomic structure and (b) calculated local density of states (LDOS) of isolated sp^2 carbon subdomain fully surrounded by nine epoxide-functional groups, (c) HOMO and LUMO levels related orbitals of atomic structure.

Morphology

The size of graphene oxide quantum dots (GOQDs) were investigated using transmission electron microscopy (TEM; JEOL 2000FX), and Atomic-force microscopy (AFM; Bruker NEOS SENTERRA AFM-Raman Spectroscopy).

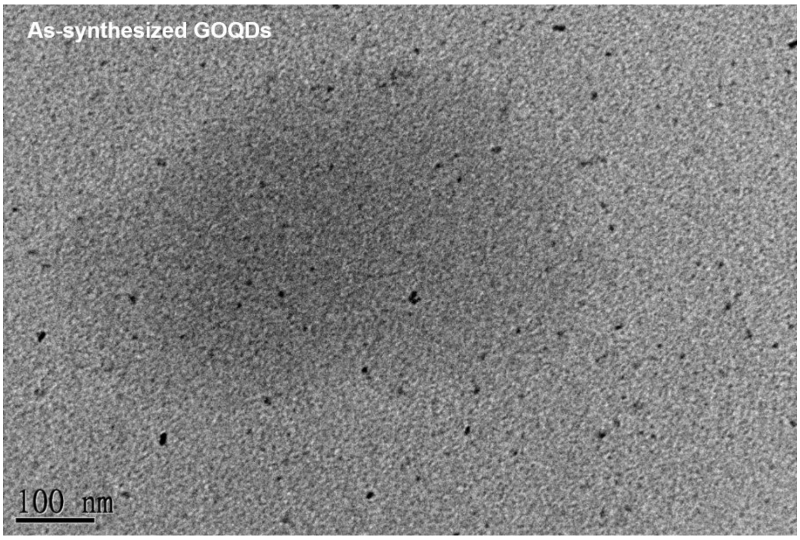

Figure S2. TEM image of as-synthesized GOQDs

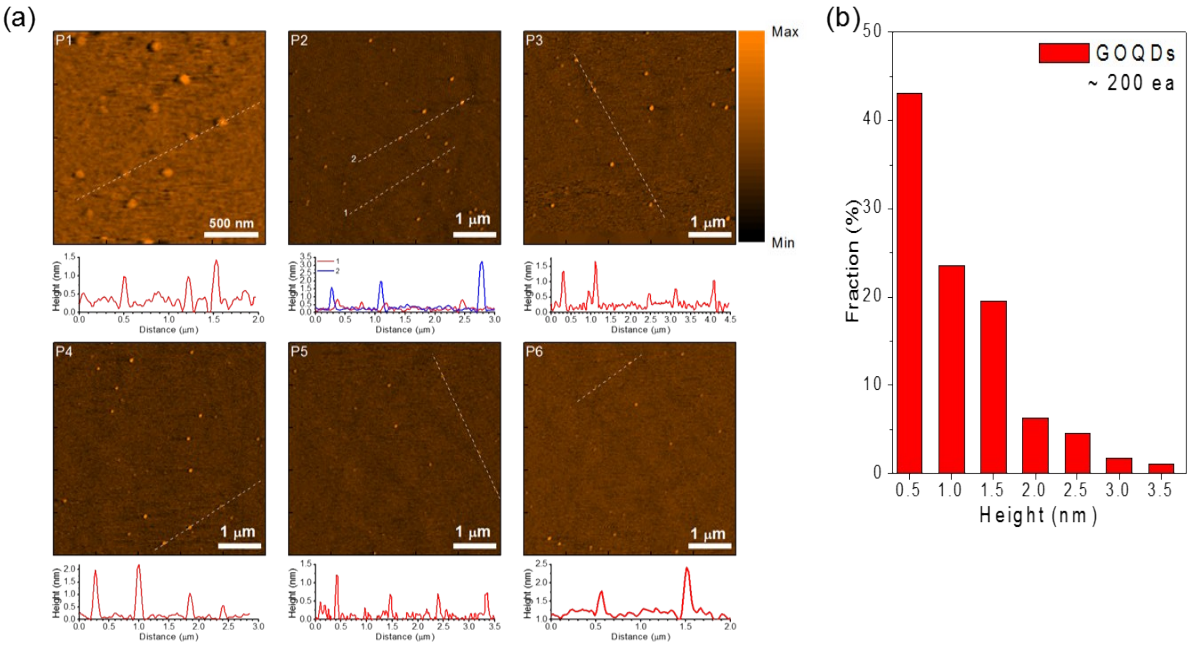

Figure S3. (a) AFM image of as-synthesized GOQDs, (b) Height distribution analysis of as-synthesized GOQDs

Raman spectroscopy

Raman spectroscopy (Bruker NEOS SENTERRA AFM-Raman Spectroscopy) were measured by using a 532 nm excitation, and the samples prepared on Si substrate. As shown in Figure S4, the Raman spectrum of as-synthesized graphene oxide quantum dots (GOQDs) shows two peaks about D-band and G-band of graphene, indicating that our GOQDs are consisted of graphitic carbon structure.

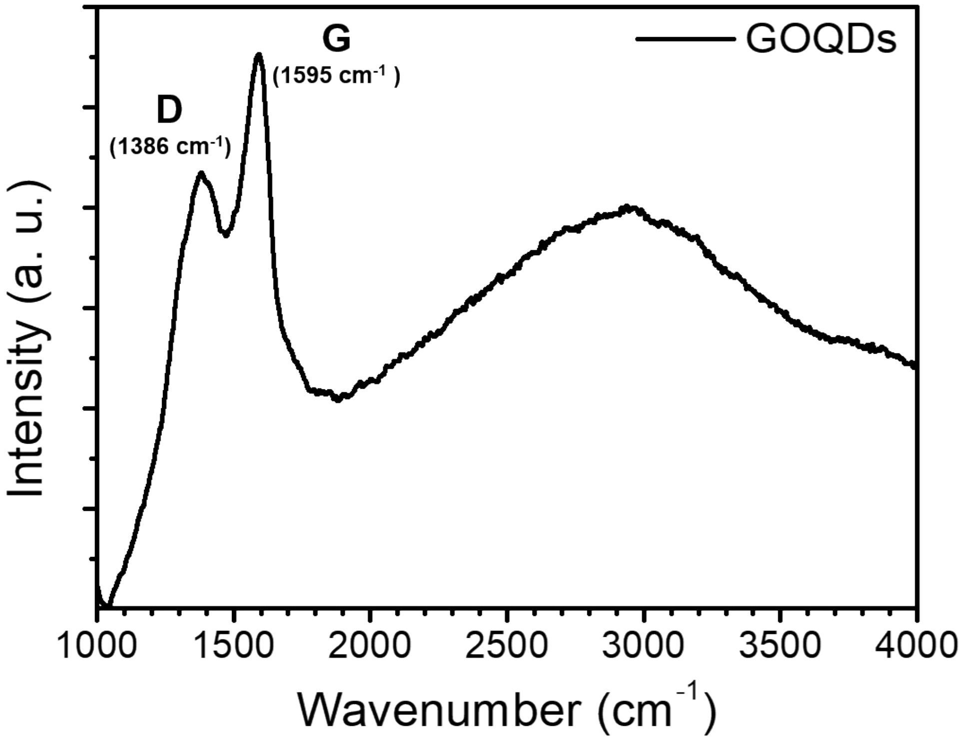

Figure S4. Raman data of the GOQDs

Photophysical properties of as-synthesized GOQDs

The UV/Vis absorption of the as-synthesized GOQDs in the deionized (DI) water shows gradual increase from 800 nm to 200 nm, and has two peaks at 225.8 nm and 295.0 nm, as shown in FigureS5 (a). The PL spectra were recorded accordingly by increasing excitation wavelengths from 250 nm to 500 nm, and then plotted as a two-dimensional (2D) PL intensity map, as shown in FigureS5 (b). FigureS5 (c) shows the PL peak position and full width at half maximum (FWHM) of the PL spectra. As the excitation change from 250 nm to 450 nm, the PL peak positions are nearly located at about 2.35 eV (528 nm) with corresponding greenish-yellow color emission. Above a 450 nm excitation, the PL peak position is the red-shift from 2.35 eV (528 nm) to 2.24 eV (554 nm). The FWHM shows the maximum linewidth at a 300 nm excitation. Besides, the FWHM also decease, corresponding to the PL red shift. From the previous literatures, these reasons were well known as the non-uniformity of the size and surface-functional groups.[2-5] In other word, since the GOQDs have the wide range of energy levels, the PL emission from the extrinsic states is reconstituted depending on the excitation energy. Furthermore, the PL spectra show the asymmetry because of the two kind of the luminescent origins: (i) intrinsic states formed by localized sp^2 carbon subdomains, (ii) extrinsic states of oxygen-functional groups and surface defects.[3,5]

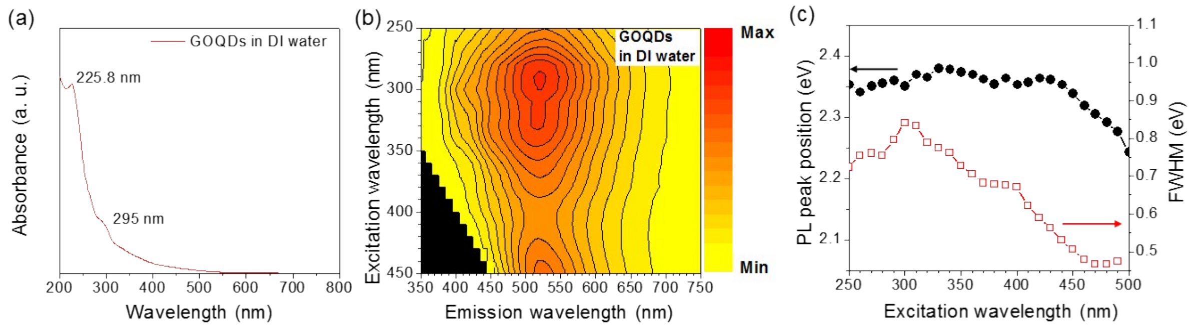

Figure S5. Optical property of the as-synthesized GOQDs in DI water: (a) Absorbance, (c) 2D matrices of PL spectra, (c) PL peak positions and full width at half maximum (FWHM) with various excitation wavelengths (λ_{ex})

Excitation energy dependent photoluminescence of as-synthesized GOQDs

Photoluminescence (PL) of the as-synthesized GOQDs excited by 280 nm, 300 nm, 320 nm, and 340 nm from Xe-lamp shows asymmetry shape because of two kind of the luminescent origins: (i) the intrinsic states formed by localized sp^2 carbon subdomains, (ii) the extrinsic states of oxygen-functional groups and surface defects. As shown in Figure S6 (a)-(d), the PL spectra are fitted by two Gaussian shaped diagrams. The fitted diagrams represent center position at about 2.9 eV (428 nm) and 2.35 eV (528 nm) with corresponding luminescent origins of intrinsic states and extrinsic states, respectively. As increasing excitation wavelengths from 300 nm to 340 nm, the portion of intrinsic PL emission is decreased. On the other hand, the PL spectra on excitation with 360 nm and 380 nm show Gaussian shaped diagram with symmetry due to disappearance of a shoulder peak at 2.9 eV (428 nm) formed by the intrinsic states.

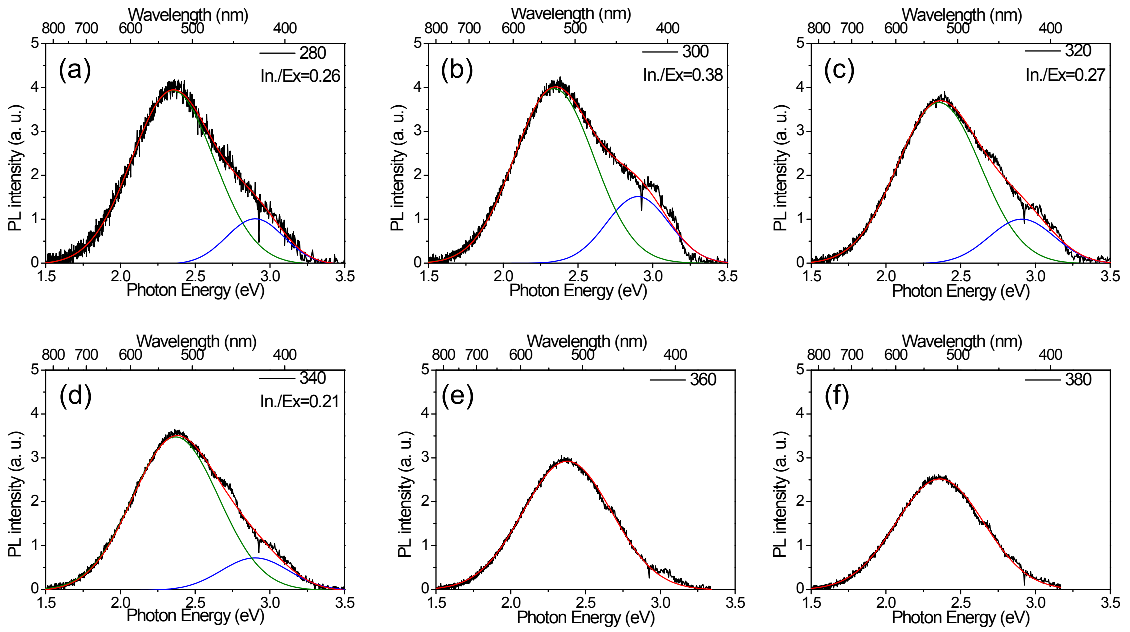

Figure S6. PL of as-synthesized GOQDs on excitation with (a) 280 nm, (b) 300 nm, (c) 320 nm, (d) 340 nm, (e) 360 nm, and (f) 380 nm. The PL spectra of (a)-(d) are fitted by two Gaussian shaped diagrams.

Time-integral PL (TIPL) of as-synthesized GOQDs

Time-resolved PL (TRPL) experiment are carried out by using Ti:Sapphire laser (Coherent, Chameleon Ultra II) and a streak camera detector (Hamamatsu, C7700-01). The excitation sources with 4 MHz repetition were prepared by third-harmonic-generation (280 nm, 300 nm, and 320 nm) and second-harmonic-generation (360 nm). As shown in Figure S7, the temporal profile of time-integral PL (TIPL) are obtained by plotting the integral PL spectra as a function of decay time (0-1 ns, 1-3 ns, 3-7 ns, 7-15 ns). As time passed for nano-second, TIPL spectra show red-shifted PL peak and decreased linewidth. This reason is different recombination time of PL emission derived from the intrinsic states (~ 430 nm) and extrinsic states (~ 530 nm).

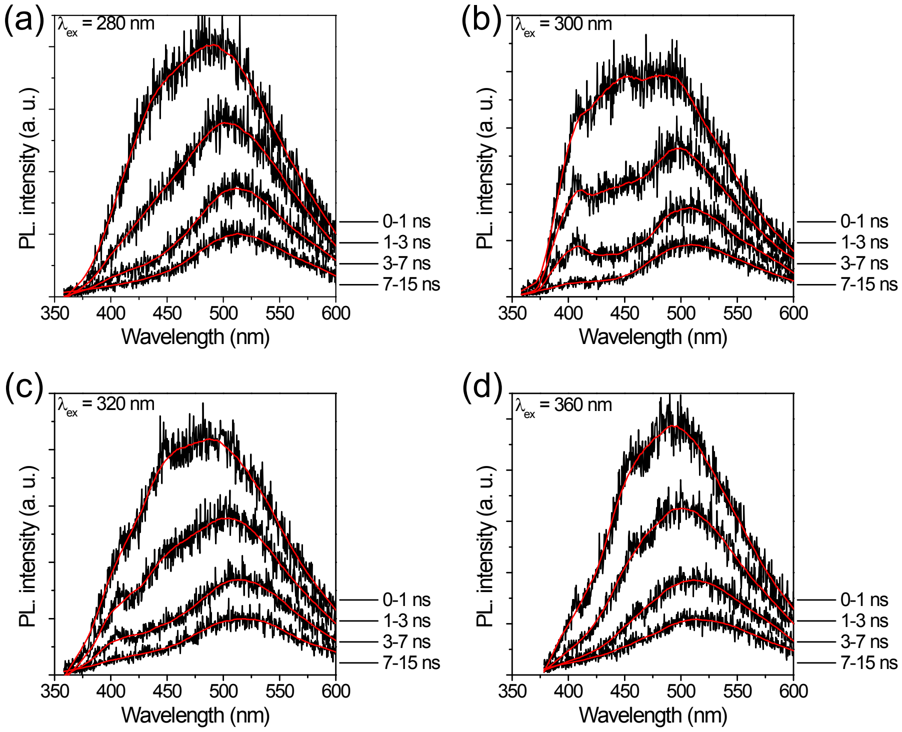

Figure S7. Time-reserved PL excited by (a) 280 nm, (b) 300 nm, (c) 320 nm, and (d) 360 nm. Temporal profile of time-integral PL spectra of the as-synthesized GOQDs as a function of recombination time (0-1 ns, 1-3 ns, 3-7 ns, 7-15 ns).

Thermogravimetric analysis (TGA)

The grafting density of the OLA on the GOQDs were estimated by thermogravimetric analysis (TGA) measurement (Table S1, Supporting Information). As a result, four different GOQDs were synthesized with the Σ values of 0 (GOQD-OLA$_N$), 0.15 (GOQD-OLA$_L$), 0.54 (GOQD-OLA$_M$), and 1.29 (GOQD-OLA$_H$) chain/nm^2, respectively.

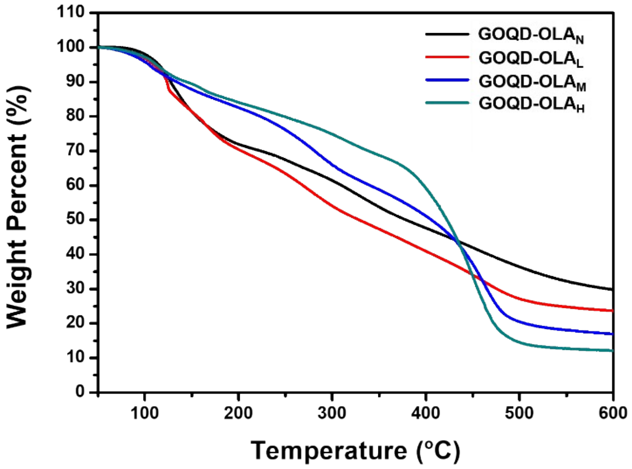

Figure S8 TGA data of GOQDs used in the present study

Table S1. Characteristic of GOQDs used in the present study

	Weight Loss Fraction below 600 °C (%)	Ligands Fraction[a] (%)	Concentration of Ligands[b] (mmol/g)	Concentration of Carbons of Graphene[c] (mmol/g)	Grafting Density[d] (chain/nm^2)
GOQD-OLA$_N$	70.20	-	-	-	-
GOQD-OLA$_L$	76.30	6.10	0.20	23.70	0.15
GOQD-OLA$_M$	83.06	12.86	0.50	16.94	0.54
GOQD-OLA$_H$	87.85	17.63	0.70	10.12	1.29

[a] Calculated from the difference in the weights loss fractions of GOQD-Alkylamine and pristine GOQDs below 650°C.

[b] The concentration of alkylamine ligands per gram of GOQD-Alkylamine.

[c] The concentration of carbons of graphene per gram of GOQD-Alkylamine.

[d] Grafting density was estimated based on the reference[10] (37.2 carbon atoms of graphene = 1 nm^2)

Fourier transform infrared spectroscopy & XPS

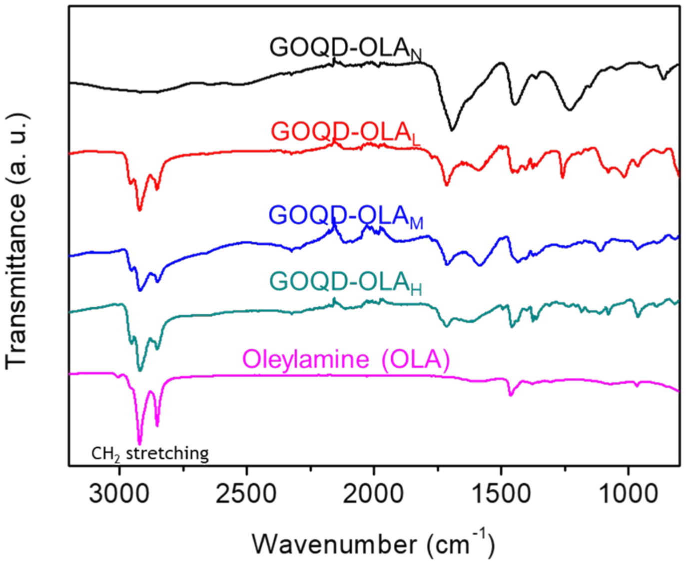

Figure S9 FTIR Spectra of various GOQD-OLA

Table S2 Calculated C/O ratio of various GOQD-OLA from XPS measurement

	GOQD-OLA$_N$	GOQD-OLA$_L$	GOQD-OLA$_M$	GOQD-OLA$_H$
C/O Ratio	1.88	3.01	3.73	4.84

Photoluminescence of tetrahydrofuran (THF) solvent

When oleylamine (OLA) grafts at the epoxide-functional groups on the GOQDs, the properties of the GOQDs were changed from hydrophilic to hydrophobic condition.[1] Hence, samples were dissolved in tetrahydrofuran (THF) solvent. As shown in Figure S9, the THF solvent has ultraviolet emission with peak at 310 nm. However, the emission of the THF do not overlap with that of the GOQDs with spectrum range between 400 nm and 700 nm.

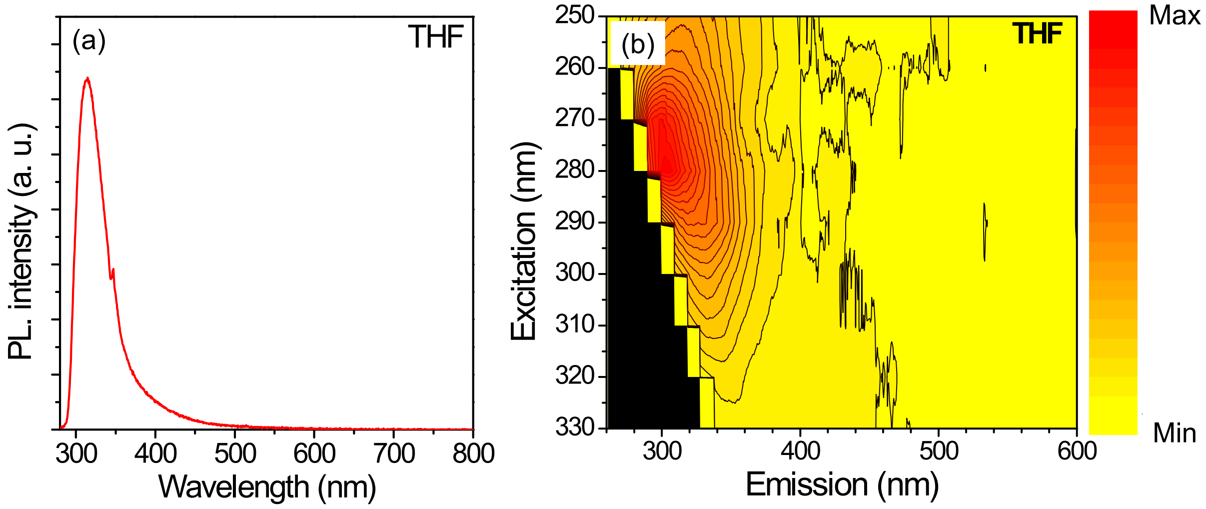

Figure S10 PL of tetrahydrofuran (THF) solvent

Photoluminescence of GOQDs in tetrahydrofuran (THF) solvent

PL emission from the GOQDs in the THF pumped by a 325 nm excitation is a blue-shift compared to them in DI water. The reason of these solvent dependent PL behavior is reported as a solvent attachment or different emissive traps on the surface.[7] Compared to the temporal profiles of TIPL spectra between the as-synthesized GOQDs in the DI water and in the THF the spectral migrations exhibit a different trend after a pump event. On the other hand, the TIPL spectra of the GOQDs in the THF show a red-shift of the PL peak position. This result suggests that the THF solvent suppress the emission from the extrinsic states of the as-synthesized GOQDs. Therefore, since the intrinsic states with the blue-color emission at about 430 nm are more predominant than the extrinsic states with the greenish yellow-color emission at about 528 nm, the PL of the as-synthesized GOQDs in the THF solvent is a blue-shift compared to that in DI water.

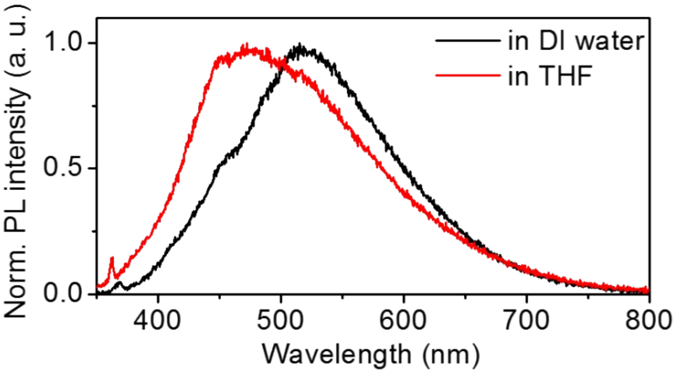

Figure S11 PL of GOQDs in tetrahydrofuran (THF) solvent

Optical properties of pure-oleylamine in tetrahydrofuran (THF) solvent

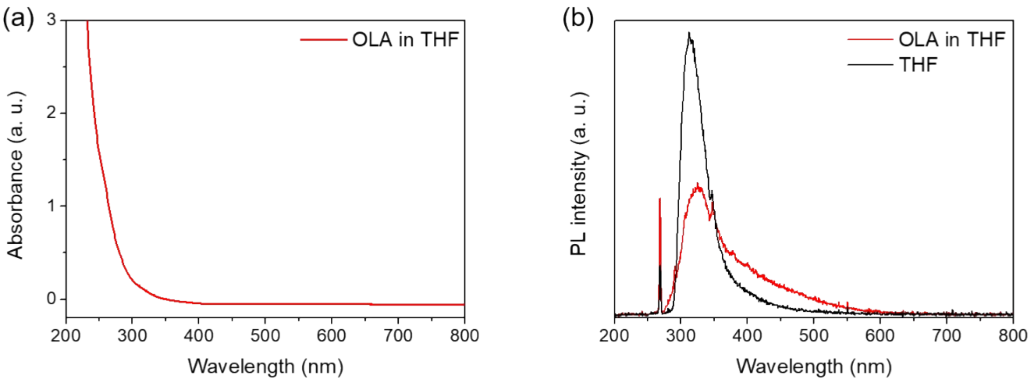

Figure S12 Optical properties of pure-oleylamine (OLA) in THF solvent, (a) absorbance, (b) photoluminescence of pure-OLA in THF and THF solvent under an excitation wavelength 266 nm.

Time-resolved PL (TRPL) of OLA-grafted GOQDs

Time-resolved PL (TRPL) experiment are carried out by using Ti:Sapphire laser (Coherent, Chameleon Ultra II) and a streak camera detector (Hamamatsu, C7700-01). The excitation sources with 4 MHz repetition were prepared by third-harmonic-generation (300 nm). the PL decay profiles are extracted from 400 nm to 600 nm in streak image. The PL decay profiles are fitted by bi-exponential function, and the fitted parameter are arranged in Table S2.

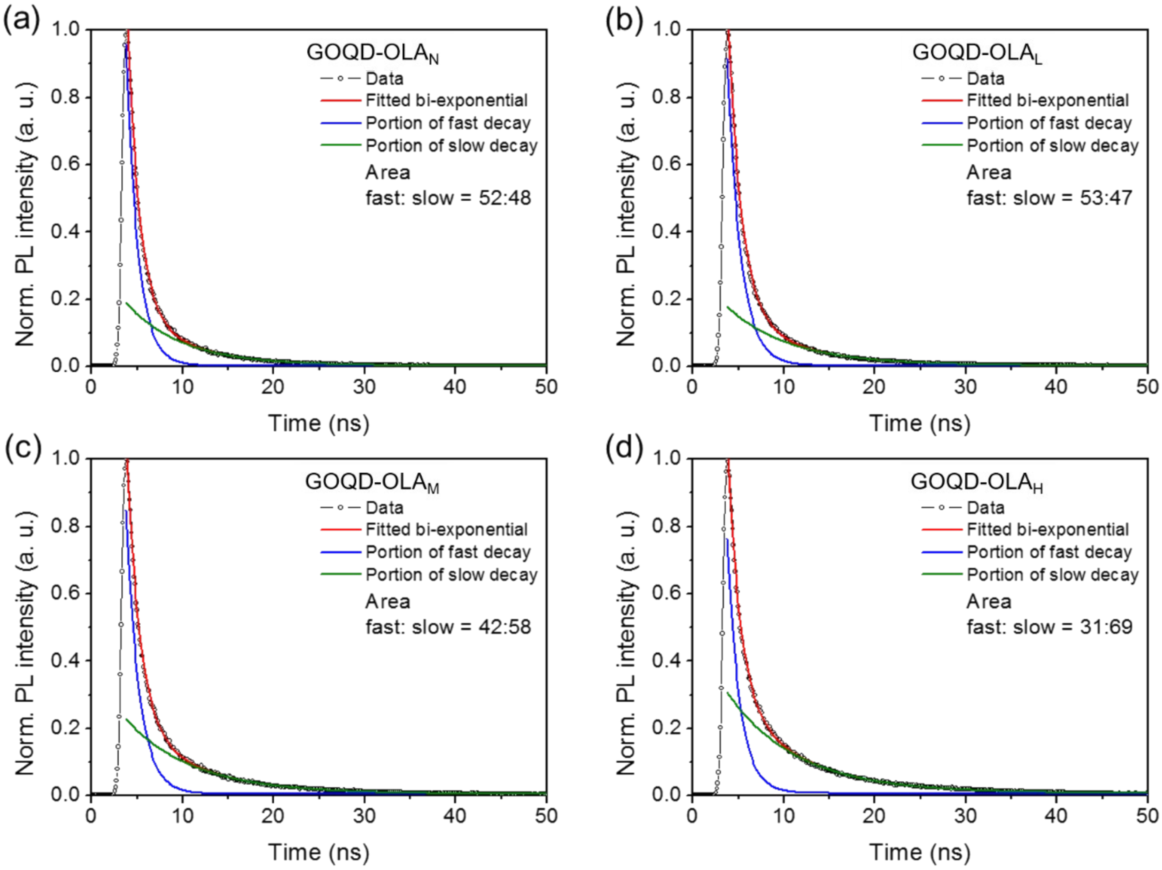

Figure S13 PL decay profiles of (a) GOQD-OLA$_N$, (b) GOQD-OLA$_L$, GOQD-OLA$_M$, and GOQD-OLA$_H$ extracted from 400 nm to 600 nm in streak image

Table S3. Lifetime of OLA-grafted GOQDs

	τ_1	τ_2	A_1	A_2	Potion of fast decay (%)	Portion of slow decay (%)
GOQD-OLA$_N$	1.31	6.16	0.980	0.020	52	48
GOQD-OLA$_L$	1.49	6.97	0.974	0.026	53	47
GOQD-OLA$_M$	1.45	7.48	0.968	0.032	42	58
GOQD-OLA$_H$	1.37	7.67	0.960	0.040	31	69
Fitted by bi-exponential equation, $y = A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2} + y_0$						

Reference

1. H. Yang, K. H. Ku, J. M. Shin, J. Lee, C. H. Park, H.-H. Cho, S. G. Jang, B. J. Kim, *Chemistry of Materials* 2016, **28**, 830-837.
2. F. Liu, M.-H. Jang, H. D. Ha, J. H. Kim, Y. H. Cho, T. S. Seo, *Advanced Materials* 2013, **25**, 3657-3662.
3. S. H. Song, M.-H. Jang, J. Chung, S. H. Jin, B. H. Kim, S. H. Hur, S. Yoo, Y. H. Cho, S. Jeon, *Advanced Optical Materials* 2014, **2**, 1016-1023.
4. H. D. Ha, M.-H. Jang, F. Liu, Y. H. Cho, T. S. Seo, *Carbon* 2015, **81**, 367-375.
5. M.-H. Jang, H. D. Ha, E. S. Lee, F. Liu, Y. H. Kim, T. S. Seo, Y. H. Cho, *Small* 2015, **11**, 3773-3781.
6. H. He, C. Gao, *Chem. Mater.* 2010, **22**, 5054
7. S. Zhu, J. Zhang, C. Qiao, S. Tang, Y. Li, W. Yuan, B. Li, L. Tian, F. Liu, R. Hu, *Chem. Commun.* 2011, **47**, 6858-6860.