Blue-Light Emissive Type II ZnO@5-Amino-2-Naphthalene Sulfonic Acid Core–Shell Quantum Dots

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Blue-light emissive type II ZnO@5-amino-2-naphthalene sulfonic acid (ANSA) core–shell quantum dots (QDs) is first fabricated. Green luminescence (GL) of 2.25 eV of ZnO QDs disappears at the threshold excitation wavelengths (λex) > 400 nm due to the electronic transition from conduction band (CB) or shallow donor centers to VZn2– at ≈0.9 eV above valence band (VB). Blue emissions from ZnO@ANSA QDs are well elucidated by the charge transfer from CB of ZnO QDs to lowest unoccupied molecular orbital (LUMO) of ANSA and from shallow donor Zn interstitial (Zni) or extended Zni states to C=O, C≡N, C=S (π*)-states, and then the electronic transitions to nonbonding C=O, C≡N, C=S (σ) states of ANSA. Spectral-dependent electron paramagnetic resonance (SDEPR) peak g = 1.96 of ZnO QDs emerges only with illumination of light shorter than 400 nm in wavelength and completely disappears in ZnO@ANSA QDs. Electrons trapped in CB or Zni’s are unveiled to participate in GL and the paramagnetic defect to derive electron paramagnetic resonance (EPR) peak g = 1.96 of ZnO. The estimated spin–spin relaxation time (T2) of ZnO QDs was about 32.5 ns, which is two orders of magnitude longer than known values for bulk or thin-film ZnO.

1. Introduction

II-VI ZnO metal oxide semiconductors have been extensively investigated as important materials in optoelectronics due to their large bandgap of 3.3 eV, large exciton binding energy of 60 meV at room temperature, and strong oscillator strength of 300 cm–1[1–3] Since the unoccupied Zn 4s orbitals in ZnO, with spherical symmetry, comprise the bottom of the conduction band, ZnO film incorporated with nanoparticles shows a high electron mobility of 10–3–10–1 cm2 V–1 s–1 and thus has been broadly adopted as an electron transport layer (ETL) in light-emitting diodes[4,5] and photovoltaic cells.[6] Owing to the excellent properties of quantum dots (QDs), such as high purity, large color gamut, and high external quantum efficiency (EQE), environmentally friendly blue emitters have been developed to implement entirely electroluminescent quantum dots LEDs (EL Qs-LEDs) displays.[7,8][15] III–V InP QDs and II–VI ZnSe QDs have emerged as Cd-free blue emitter QDs. InP QDs have shown EQE of 21.4% and lifetime[9] comparable to that of Cd-based QDs, but still have quite a long wavelength as blue emitters and low photoluminescence quantum yield (PLQY) of 76%.[10] Several ZnSe1–xTe alloyed QDs have been synthesized[11–14] and, lately, ZnTeSe/ZnSe/ZnS core–shell–shell QDs have shown blue emission tuned at 457 nm by Te doping. EQE of up to 20.2% with brightness of 88 900 cd m–2, and T50 = 15 850 h at 100 cd m–2.[15] Besides the rarity and mild toxicity of the element Te, the tendency of Te-containing compounds toward oxidation reduces chemical stability and thus lowers emission efficiencies. On the other hand, as an alternative to ZnSeTe material to overcome these potential drawbacks of Te, ecofriendly II–VI ZnO QDs will be good candidates. The visible emissions of ZnO QDs including nanostructures, films, and single crystals have been known to be related to intrinsic defect centers.[16–18] As far as the GL is concerned, despite a vast number of investigations, its nature is yet to be understood and GL is widely explained by the transition of photoexcited electrons from CB or shallow donors to deep oxygen (V0) or zinc (VZn0) vacancies.[19,20] In the case of blue luminescence (BL) it is believed to correlate with the electron transition from shallow donors to deep acceptor levels of zinc vacancies (VZn0) or interstitial oxygen (Oi) or VB.[21,22] We come to the conclusion that various centers may be involved in visible luminescence simultaneously, compared with band-to-band transition in the case of UV emission.
It is well known that as the size of ZnO QDs decreases, the intensity of GL increases due to the increase of the surface to volume ratio. This indicates the GL is related with defects located at the surface. Therefore, the control of visible emission can be achieved by hybridization of defect centers localized on the surface of ZnO with other materials. As inorganic semiconductor/organic hybrids structures, ZnO QDs with fluorophores such as anthracene (C14H6O) and the fluorescent dye AlexaFluor 594 (A954) cadaverine were previously prepared and excited energy transfers from donors to acceptors were well described by dipole–dipole coupling at the interface. Moreover, various hybrid nanostructures between ZnO QDs and nanocarbons such as ZnO-graphene QDs (QGDs), ZnO-C60, ZnO/GO, ZnO-rGO have been reported and variations of PL have been correctly ascribed to interfacial charge transfer from CB or trapping states of ZnO to nanocarbons. Such inorganic semiconductor–organic heterojunctions can typically be classified as type-I or type-II, depending on the relative alignment of the CB and VB edges of ZnO with the LUMO and highest occupied molecular orbital (HOMO) of the organic materials that are combined at the heterointerface. Recently, type I ZnO@GO core–shell QDs with CB (−3.22 eV) of ZnO lower than LUMO (−3.09 eV) of GO and VB (−6.71 eV) of ZnO QDs higher than HOMO (−7.51 eV) of GO were reported. ZnO@GO core–shell QDs showed only blue luminescence (BL), without green or yellow emission, irrespective of the excitation wavelength of λex = 300–410 nm; surface defects existing on the surface of the ZnO QDs were mostly eliminated by hybridization of Zn with oxygen functional groups of GO. The higher energy states induced by oxygen-related functional groups in GO in close vicinity (10 nm) to inner ZnO QDs acted as donors for Frenkel pair blue emission from Zn2− donor level (D) to Vzn acceptor level (A). The proximity of these resonant energy levels gives rise to nonradiative transfer of electron excitations from GO shell to inner ZnO QDs core. In addition, other, type II core–shell QDs can be suggested as a way of aligning the CB of ZnO QDs with the lower level of LUMO and the VB of ZnO QDs with lower or higher energy level of HOMO of organic shell materials. Among PAHs, acenes, a class of organic compounds made up of linearly fused benzene rings (benzene, naphthalene, anthracene, tetracene, and pentacene (Cn+1H2n, n = 1–5)) have simple molecular and electronic structures with well-defined LUMO and HOMO energy levels, which can be also calculated by density functional theory (DFT). In this study, Zn-rich ZnO QDs were synthesized by solution precipitation and hybridized with a simply structured f-PAH, ANSA (H2NCOH2SO3H) with O, N, and S containing functional groups as type II ZnO@ANSA core-shell QDs. Electronic energy levels of CB and VB, and defect states in ZnO and those of the LUMO, HOMO, and levels induced by functional groups of amines (−NH2) and sulfonic acid (S=O) in ANSA are precisely determined using an ultraviolet photoemission spectroscopy (UPS), photoluminescence excitation (PLE), UV–VIS absorption spectroscopy, and DFT. By comparison of resonant energy levels between ZnO core and ANSA shell, the enhanced blue emissions centered at around 440 and 480 nm in the type II ZnO@ANSA core–shell QDs are well elucidated by charge transfer from CB of ZnO QDs to LUMO of ANSA and from Zn2+/ex-Zn to antibonding O, N, and S (π*) states, and then the subsequent electronic transitions to nonbonding states. Followed by the reason Type-II core–shell QD is preferred in this study. Up to now, the intrinsic defects causing GL of ZnO and the relevance of GL with the electron paramagnetic resonance (EPR) signal g = 1.96 are still controversial. From SDEPR over ZnO QDs, it has been definitely revealed that the EPR peak g = 1.96 was only observed with light illumination of λ < 410 nm, which is coincident with the threshold wavelength of GL in ZnO QDs. After hybridization of ZnO with ANSA, the EPR peak g = 1.96 completely disappears; instead, a wholly new value of g = 2.06, related to the free radical of ANSA, emerges regardless of excitation wavelength. So, it is clearly suggested that the paramagnetic defect used to induce the EPR signal g = 1.96 is directly related to the photoexcited electrons captured in CB or shallow donors in ZnO QDs.

2. Results and Discussion

Figure 1a shows the survey spectra of ZnO QDs and ZnO@ANSA hybrid QDs. The functional groups of the sulfonic acid (S=O)−OH and the amine (−NH2) are clearly identified by the occurrence of S2p at around the binding energy (BE) of 168 eV and N1s at BE = 400 eV and the atomic contents of S and N are estimated to be as much as 2.16 % and 2.8%, respectively, as listed in Table S1, Supporting Information. Figure 1b shows Cls core-level spectra for ZnO QDs, ANSA, and ZnO@ANSA hybrid QDs; their fitted subpeaks are presented in Figure S1 and Table S2, Supporting Information. C1s for ZnO QDs is resolved into three subpeaks at BE = 284.6, 286.27, and 288.18 eV, which correspond to C−CH3, N−CH3/OH−CH3 from TMAH, and the acetoxy group of O−(−CH3)=O, respectively. Acetoxy and TMAH-related groups remaining on the surface of ZnO QDs are almost removed when dissolved in DMF for hybridization with ANSA. As shown in Figure S1 (Cls), Supporting Information, C1s of ANSA is also resolved into C−C/−CH3 (284.67 eV), C−S/−C−N (283.30 eV), and a satellite peak (π−π*) at BE = 290.60 eV. Based on Cls fitting of ZnO and ANSA, Cls of ZnO@ANSA core−shell QDs can be similarly fitted into three subpeaks of C−C/−CH3 (284.61 eV), C−S/−C−N (285.74 eV), and O−C−(CH3)=O (288.32 eV). O1s of ZnO@ANSA shows a feature very similar to that of ZnO QDs (Figure 1c), but it is noticeable that the chemical shift toward high BE occurs after hybridization of ZnO QDs with ANSA. This indicates the electron transfer from ZnO QDs to ANSA. As shown in Figure S1 (O1s), Supporting Information, O1s for ZnO QDs can consist of lattice O as Zn−O, hydroxyl Zn−OH (530.82 eV), and carboxylate in O−(−CH3)=O (531.39 eV). O1s peak of ANSA is explicitly divided into hydroxyl group (S−OH) at BE = 532.66 eV and carbonyl group (S=O) at BE = 531.54 eV of OH−S(=O)2. In the case of the Zn2p core-level peak, spin−orbit splitting of ΔSO = 23.1 eV between Zn2p1/2 and Zn2p3/2 (1043.58–1020.48 eV) for ZnO QDs is the same as that of ZnO@ANSA core−shell QDs (Figure 1d), but Zn2p of ZnO QDs peak is blue-shifted as ΔE = 1.4 eV in ZnO@ANSA core−shell QDs, which means that electrons are transferred from inner Zn (donor) core to outer ANSA (acceptor) shell. N1s peak (Figure 1e) of ANSA is observed at around BE = 401.67 eV with a full width at half maximum (FWHM) of 1.77 eV and is believed to be derived from C−NO2 (var2, (atm. = aromatic). This peak
moves toward low BE at 399.88 eV, more accurately moving at $\text{BE} = 400.02 \text{eV}$ (FWHM = 2.66 eV) after background subtraction and fitting of as much as $\Delta E = 1.67 \text{eV}$ in ZnO@ANSA core–shell QDs (Figure S1 (N1s), Supporting Information). This redshift in BE and broadening in FWHM of N1s peak clearly support that hybridization between ZnO QDs and ANSA is attained by $\text{C–NH(arom.)}$ bond instead of sulfonic acid bond and electrons are transferred from ZnO (donor) to ANSA (acceptor), which is coincident with the blue shift of $\Delta E = 1.4 \text{eV}$ of Zn2p in the above. On the other hand, the S2p peak (Figure S1 (S2p), Supporting Information) at BE = 168.59 eV for ANSA can be resolved into spin-orbit splitting terms $\Delta_{\text{SO}}$ of S2p$_{1/2}$ at BE = 170.66 eV and S2p$_{3/2}$ at BE = 168.46 eV, respectively, which values are consistent with the fully oxidized sulfur like $\text{SO}_3^{2-}$ or $\text{SO}_4^{2-}$ observed by XANES.[39,40] In the S2p spectra for ZnO@ANSA, two components at BE = 161.60 and 168.5 eV are observed and the difference of 6.9 eV in BE agrees with that of 6.1 eV from the previous report.[41] The former peak can be assigned to $\text{Au-S}$, indicating the presence of metal sulfides[42] or S-Au of self-assembled monolayer.[43] Such a small change of 0.09 eV in BE of S2p peak related to oxidized sulfur means that no chemical bonding occurs between sulfonic acid and ZnO. As illustrated graphically in Figure 1g, it can be said when ZnO QDs react with ANSA, Zn-NH bond is formed by chemical reaction between hydroxyl bonding of Zn$_2$O$_2$/C$_0$OH on the surfaces of ZnO QDs and the amino group (-NH$_2$) through dehydration. On the other hand, S(=O)$_2$–OH on ANSA remains without reacting with $\text{-OH}$ on ZnO QDs. ZnO QDs and ZnO@ANSA core–shell QDs emit yellow luminescence (YL) and blue luminescence under UV lamp ($\lambda = 365 \text{nm}$).

**Figure 1.** XPS a) survey spectra, b) C1s, c) O1s, d) Zn2p, e) N1s, and f) S2p core level spectra for ZnO, ANSA, and ZnO@ANSA core–shell QDs. g) Schematic diagram of chemical reaction between ZnO and ANSA. h) Photographic images of ZnO and ZnO@ANSA core–shell QDS irradiated by UV lamp ($\lambda = 365 \text{nm}$).
were recorded using an X-ray diffractometer (MD-10) with Cu Kα radiation of wavelength $\lambda = 1.5406 \text{Å}$ in the scan range $2\theta = 20°$–$80°$. The diffraction peaks observed at $2\theta$ values of 31.94°, 34.38°, 36.18°, 47.6°, 56.78°, 62.86°, and 68.08°, can be indexed to different planes of crystalline ZnO with wurtzite structure, as illustrated in the Figure 2a (JSPDF file no. 79-2205). ANSA shows many sharp diffraction peaks, indicating that ANSA has microcrystalline-like structure. In ZnO@ANSA core–shell QDs, most XRD peaks except three peaks related to [100], [002], and [102] planes are mostly suppressed and not well distinguished. As a result of ZnO QD formation, described in Figure 2b, hydroxyl (–OH) as well as acetoxy (–O–C=O–CH3) groups existed on the surface of ZnO QDs, which is confirmed by the observation of absorption peaks at 1560 and 1400 cm$^{-1}$ (COO–), and at 3400–3200 cm$^{-1}$ (OH). In addition, the occurrence of absorption peaks at 1490 and 1330 cm$^{-1}$ corresponding to C–N bonding of TMAH indicates the remains of the basis product of TMAH within ZnO QDs, even after washing with acetone. These peaks almost disappear after the outer shell of ANSA reacts with the interface of ZnO QDs in DMF through heating at 100 °C, as shown in Figure 2b. In the case of ZnO@ANSA core–shell QDs, aromatic C–H stretching mode (2920, 2850 cm$^{-1}$), aromatic C=C bond (1630, 1530 cm$^{-1}$), and N–H stretching mode (960 cm$^{-1}$) are clearly observed and O–H stretching mode and C–N bond of TMAH disappear. In the Figure S2, Supporting Information, HRTEM images of ZnO QDs show a statistical distribution with average size of ≈4.8 nm. The lattice spacing of 0.244 nm corresponds to the interplanar distance of the (101) crystal plane of wurtzite ZnO. Figure 2c presents energy-dispersive X-ray spectroscopy (EDX) images of ZnO@ANSA QDs showing a statistical distribution with average size of ≈6.1 nm. EDX-elemental mapping images explicitly illustrate the C, Zn, S, and O atoms of ZnO@ANSA core–shell QDs.

Figure 3 shows Tauc plot $(\alpha h\nu)^2$ vs $h\nu$ obtained from UV–vis absorption spectrum of ZnO QDs using the following Equation (1).

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

where $\alpha$ is an absorption coefficient, $h$ is Planck’s constant, $\nu$ is photon frequency, $A$ is a constant relating the effective mass

![Figure 2](https://example.com/figure2.png)

**Figure 2.** a) XRD pattern and b) FT-IR spectra of ZnO and ZnO@ANSA core–shell QDs. HRTEM images of c) ZnO@ANSA core–shell QDs.
associated with valence and conduction bands, and $E_g$ is optical bandgap. From the Tauc plot, the bandgap ($E_g$) for ZnO QDs is found to be 3.4 eV by extrapolating the linear part until it intersects with the $h\nu$ axis. From the effective mass approximation (EMA) model considering the quantum confinement, the Coulomb interaction, and the spatial correlation between electrons and holes, the increase of the bandgap of QDs can be theoretically described as in the Equation (2)[44,45]

$$E_{(g,QD)} = E_{(g,bulk)} + \frac{h^2}{8R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.78e^2}{4\pi\varepsilon_0\varepsilon_r R} - 0.248E_{hyd}$$

where $E_{(g,QD)}$ and $E_{(g,bulk)}$ are bandgaps of QDs and bulk ZnO, respectively. $h, \hbar, \varepsilon_r = 3.7$, and $E_{hyd}$ are QD radius, Planck's constant, dielectric constant at optical frequency, and bulk exciton binding energy (60 meV), respectively; $m_e^* = 0.24m_0$ and $m_h^* = 0.59m_0$[46] are the effective mass of electrons and holes, respectively. By adopting the above Equation (2), the theoretical bandgap for ZnO QDs with $R = 2.4$ nm is determined to be $E = 3.45$ eV, which is coincident with the value 3.4 eV obtained from excitonic emission captured from NBE at 369 nm (=3.36 eV) of photoluminescence spectra, which is usually lower than the CB by the value of exciton binding energy (60 meV).

As shown in Figure 4a, PL for ZnO QDs shows GL centered at 551 nm (2.25 eV) and near band edge emission (NBE). The notch observed at around 550 nm comes from changing band-pass filter (BPF) with center wavelength from 360 to 540 nm in the spectrofluorometer, which does not mean that there is an error in the PL measurement result. The ZnO QDs emit a yellow color when exposed to radiation from a 365 nm UV lamp (see the inset in Figure 4a). NBE and visible emissions in ZnO are well-known to have an excitonic nature and to result from intrinsic defects,[47] As shown in Figure 4b, NBE peaks are centered at around 369 nm (3.36 eV). As $\lambda_{ex}$ increases, GL intensity gradually increases and reaches a maximum at $\lambda_{ex} = 360$ nm (3.44 eV), but starts to decrease from $\lambda_{ex} = 370$ nm (3.35 eV). All of the GL intensity values at $\lambda_{ex} = 390$ nm (3.18 eV) and 400 nm (3.10 eV) are very low but still observable. The GL almost disappears at $\lambda_{ex}$ longer than 400 nm and only the blue emission remains at 460 nm for $\lambda_{ex}$ longer than 400 nm and only the blue emission remains at 460 nm for $\lambda_{ex}$ longer than 400 nm and only the blue emission remains at 460 nm for $\lambda_{ex} = 410$–430 nm. This implies that the threshold excitation wavelength ($\lambda_{th}$) or energy ($E_{th}$) for GL is $\lambda_{th} < 400$ nm ($E_{th} > 3.1$ eV). As shown in Figure 4c, BL is clearly

![Figure 3. Tauc plot obtained from UV–vis absorption spectrum of ZnO QDs.](image)

![Figure 4. a) PL of ZnO QDs at various excitation wavelength ($\lambda_{ex}$). b) Enlarged view of NBE region denoted as A. c) Enlarged view of PL at $\lambda_{ex} = 390$–430 nm. d) Gaussian fitting of PL obtained at $\lambda_{ex} = 340$ nm. e) PLE spectra for $\lambda_{Det} = 370, 465, 530$, and 580 nm excited at $\lambda_{ex} = 340$ nm. f) Gaussian fitting of PLE for $\lambda_{Det} = 465$ nm excited at $\lambda_{ex} = 340$ nm.](image)
confirmed by the new occurrence of a sharp peak at around \(\approx 460\) nm after the disappearance of GL at the longer excitation wavelengths of \(\lambda_{ex} = 410–430\) nm. The visible emission peak (Figure 4d) produced at \(\lambda_{ex} = 360\) nm can be further resolved into three subpeaks centered at 465 nm (2.66 eV), 535 nm (2.31 eV), and 580 nm (2.13 eV). From the PLE spectra for ZnO QDs (Figure 4e), the detection wavelengths (\(\lambda_{det}\)) of 535 and 580 nm are produced by several energy levels of 270 nm (4.59 eV), 325 nm (3.81 eV), and 350 nm (3.54 eV) belonging to the resonant energy levels in CB, and 360 nm (3.44 eV), corresponding to CB. The resonant energy levels near CB are consistent with the result that CB is composed of mainly O2p-Zn4s, 4p hybridized orbitals.\(^{[1,48]}\) However, the BL of \(\lambda_{det} = 465\) nm is additionally excited by the energy level of 428 nm (2.89 eV), as shown in Figure 4f. Considering the excitation energy level at 428 nm, it is quite natural that the BL of 465 nm (2.66 eV) is inevitably ascribed to the electronic transition from the energy level of 2.89 eV (428 nm) to the energy level of 0.23 eV (2.89–2.66 eV) from the VB, which is well-known as a deep acceptor of Zn vacancies (\(V_{Zn}\)).\(^{[48–50]}\) These results indicate that GL and BL directly depend on the excitation wavelength and have different luminescence mechanisms. In the case of GL, \(E_{ex}\) should be larger than 3.10 eV (\(\lambda_{ex} = 400\) nm), for which the energy region corresponds to the super-\(E_{g}\) excitation energy and very shallow donor levels are located within 0.3 eV below CB. On the other hand, BL can be observed only at excitation energy less than \(E_{ex} < 3.02\) eV (410 nm), which is referred to as sub-\(E_{g}\) excitation energy.\(^{[51]}\) In this sub-\(E_{g}\) excitation range of \(E_{ex} < 3.0\) eV (410–430 nm), it is worthwhile to note that no emissions related with green, yellow, or red are detectable in the PL spectra, although \(E_{ex} = 410–430\) nm (2.88–3.02 eV) is large enough for electrons to be excited into \((V_{O})^+\) (2.35–2.39 eV) and \((V_{O})^{2+}\) (1.28–1.39 eV) from VB; these have been widely known as defect levels that participate in green or yellow emission within the bandgap.\(^{[20,52]}\) The dominant low-energy peak at 4.28 eV located \(\approx 0.5\) eV below CB was in particular assigned to extended interstitial Zn (ex-Zn)\(^{[53]}\) and the shallow acceptor located at around \(\approx 0.3\) eV from VB is also well known as Zn vacancies (\(V_{Zn}\)).\(^{[54,55]}\) The shallow acceptor at 0.23 eV is very close to \(V_{Zn}^+\) of 0.18 eV, obtained by theoretical calculation.\(^{[56]}\) As a consequence, GL of 535 nm (2.31 eV) and 580 nm (2.13 eV) correlate with the electronic transition from CB (3.4 eV) or \(n_{V_{Zn}}\) (\(\approx 3.1\) eV) to deep levels at 1.09 eV (3.4–2.31 eV) or 0.97 eV (3.1–2.13 eV); BL of 465 nm (2.66 eV) originates from the electronic transition from ex-Zn (2.89 eV) to \(V_{Zn}^+\) (0.23 eV). Related to GL, deep levels at 0.97–1.09 eV are very close to \(\approx 0.9\) eV, known as a value common to \(V_{O}^+\) or \(V_{O}^{2+}\).

The defect center of GL in ZnO QDs can be further described in relation with Zn (\(V_{Zn}\)) or oxygen (\(V_{O}\)) vacancies. Regarding \(V_{O}\), the GL of ZnO has been suggested as stemming from electron-hole radiative recombination at the \(V_{O}\) center,\(^{[50]}\) but its proper optical transition process and the exact energy level of \(V_{O}\) is still not reasonably elucidated. Estimated transition levels of \(e (2+/+)+e (+/0)\), calculated using LDA + U for \(V_{O}\) in ZnO, are 2.51 and 1.82 eV from VB,\(^{[50]}\) respectively; these values show discrepancies to a certain extent from 2.89 eV (ex-Zn) and \(\approx 0.9\) eV from VB in the present PL. These results confirm that GL is not generated through \(e–h\) recombination between photoexcited electron in oxygen vacancy defect centers (\(V_{O}^+\), \(V_{O}^{2+}\)) and holes existing in VB. In relation to \(V_{Zn}\), GL has been proposed to occur due to the electronic transition between CB and a shallow donor, or from two excited donor levels\(^{[58]}\) to \(V_{Zn}\). In particular, it was reported\(^{[59]}\) that two deep bands of YL at 2.35 ± 0.05 eV and GL at 2.53 ± 0.05 eV could be attributed to \(V_{Zn}\) and \(V_{O}\), respectively. YL is consistent with the GL of 2.25 eV (2.13–2.31 eV) in the present ZnO QDs. The LDA- and LDA + U-based extrapolation approach predicted acceptor levels of 0.18 and 0.87 eV\(^{[52]}\); also, first-principle pseudopotential calculation predicted the energy level of \(V_{Zn}\) at \(0.8\) eV from the VB.\(^{[20]}\) The transition levels of \(\epsilon (–1/–2)\) and \(\epsilon (0/–1)\) occur at 0.87 and 0.18 eV above VB; these are very similar to 0.9 and 0.19 eV extracted from the present PL. Hence, these two acceptor levels of \(V_{Zn}^-\) and \(V_{Zn}^{2–}\) can be properly assigned to 0.19 and 0.9 eV from VB, respectively. The validity of the \(V_{Zn}\) and \(V_{O}\) models will be discussed later in combination with the SDEPR spectroscopy results.

As can be seen in Figure 5a, PL for ANSA consists of two prominent peaks of UV emission at 340 nm, as well as BL centered at around 452 nm. From the Gaussian fitting of PL excited at \(\lambda_{det} = 300\) nm (Figure 5b), UV emissions are resolved into three subpeaks at 325, 335, and 356 nm and BL is fitted by two subpeaks of 446 nm (2.78 eV) and 472 nm (2.62 eV). Prior to the description of the PL for ANSA, we would like first to analyze the UV-Vis absorption spectrum of ANSA, in Figure S3a, Supporting Information, in which seven distinctive peaks can be seen at around 267 nm (4.64 eV), 277 nm (4.47 eV), and 289 nm (4.29 eV), with high intensity, and at around 308 nm (4.02 eV), 315 nm (3.93 eV), 322 nm (3.85 eV), and 362 nm (3.42 eV) with relatively low intensity. In the high intensity region, the peak at 277 nm corresponds to \(\pi\) (HOMO, \(C=C\)) (–7.92 eV)–\(\pi^*\) (LUMO, \(C=C\)) (–3.45 eV) transition, a shoulder peak at 289 nm with weaker intensity resulting from nonbonding \(n\) state \(\pi\) (–7.74 eV)–\(n^*\) (LUMO, \(C=C\)) transition, and that at 267 nm from \(\pi\) (HOMO, \(C=C\)) to the resonant energy level in the \(\pi^*\) (LUMO, \(C=C\)) transition located at –3.28 eV from the vacuum energy level (\(E_{vac} = 0\) eV). (The reference energy levels of HOMO (–7.92 eV) and LUMO (–3.45 eV) are determined by using UPS and will be discussed as below.) In the low intensity region, the three peaks at 308, 315, and 322 nm can be regarded as reflecting the absorption between the \(\pi\) (HOMO, \(C=C\)) and induced \(\pi\) (\(n^*\)-state), \(n\) (\(\pi^*\)-state), and \(S\) (\(\pi^*\)-state) located below LUMO at –3.90, –3.99, and –4.07 eV from the \(E_{vac}\), respectively. The absorption edge crossed by the \(x\)-axis at 362 nm (3.40 eV) can be plausibly explained by two transitions: the nonbonding state \(\pi\) (–6.85 eV)–\(\pi^*\) (LUMO, \(C = C\)) transition or the nonbonding state \(\pi\) (–7.74 eV) to nonbonding \(\pi^*\) (–4.32 eV) transition. From the ANSA absorption spectra, it can be reasonably assumed that the two non-bonding \(\pi\) states and four nonbonding \(\pi^*\) states existed between the LUMO (\(C=C\)) and HOMO (\(C=C\)) energy levels and corresponding energy levels of ANSA can be approximately depicted as shown in Figure S3b, Supporting Information.

From the fitting of PLE for ANSA as shown in Figure S5c, the \(\lambda_{det} = 440\) nm is well resolved into five excitation energy levels of 265 nm (4.67 eV), 279 nm (4.44 eV), 290 nm (4.27 eV), 317 nm (3.91 eV), and 334 nm (3.71 eV). These subpeaks are almost consistent with those of the UV-Vis absorption spectra, except for the excitation centers of 317 and 334 nm, which correspond to low
intensity regions in the UV-Vis spectra. Similar to the UV–vis spectra, the excitation centers at 317 and 334 nm in PLE can be assigned to adsorption from HOMO (π, C=C) (−7.92 eV) to nonbonding π*-states at −4.01 and −4.21 eV, respectively. Accordingly, the two fitted BL peaks at 446 and 472 nm can be successfully ascribed to the electronic transition from nonbonding π*-state at −4.01 and −4.21 eV, respectively, to nonbonding π-state at −6.85 eV. Meanwhile, the PL for ZnO@ANSA core–shell QDs in Figure 5d shows one BL peak centered at around 440 nm. This BL peak is resolved into two subpeaks centered at 437 and 478 nm (Figure 5e), which are similar to the 446 and 472 nm peaks for ANSA. From the fitting of PLE for ZnO@ANSA core–shell QDs in Figure 5f, the BL peak at 445 nm is excited by five energy levels of 260 nm (4.76 eV), 310 nm (4.0 eV), 330 nm (3.75 eV), 350 nm (3.54 eV), and 420 nm (2.95 eV). Compared with the PLE of ANSA at λDet = 440 nm, the resolved excitations of 260, 310, and 330 nm are related to those of ZnO QDs, but that of 350 nm seems to be related to those of ZnO QDs, judging from the sudden increase of the intensity at 350 nm, as for ZnO (Figure 4e). Moreover, as shown in the inset of Figure 5f, the last emission of 420 nm is certainly related to the energy level of 428 nm (ex-Zn) which participates in the BL of the ZnO QDs.

Figure 6a,b shows UPS spectra of ZnO QDs and ANSA. Based on the UPS experiment, the work function (φ) of ZnO QD and ANSA was defined as the energy difference between the vacuum level (Evac = 0 eV) and the Fermi energy (EF). This was determined to have values of 3.35 and 4.27 eV, as shown in Figure 6a,b by extrapolating the cutoff curve of the kinetic energy of secondary electrons using the relation φ = hv − (E_{cutoff} − E_F), where hv = 21.22 eV (corresponding to the He I UV resonance line). Moreover, VB is also acquired using the relationship VB = 21.22 − (E_{cutoff} − E_{inset}), where E_{inset} is the energy onset in the VB region. This was determined to be 3.4 eV for ZnO QDs and 3.65 eV for ANSA, and thus VB for ZnO QDs and HOMO for ANSA are estimated to be −6.75 and −7.92 eV from Evac. From the UPS, PL, and PLE spectra, an Anderson electronic energy diagram can be created, as shown in Figure 6c, where the x-axis is plotted against the vacuum level (E_{vac}) as a reference of E_{vac} = 0 eV. From Figure 6c, GL of ZnO QDs can be defined as the electronic transitions for CB or shallow donors (Zn) to deep donor V_{Zn} 2− and BL as that from shallow donor ex-Zn, to deep donor V_{Zn} , which means that both GL and BL can be satisfactorily modeled by the V_{Zn} model. In the case of ANSA, the electronic transitions from nonbonding π*-states (−4.01 and −4.21 eV) to nonbonding π-state (−6.85 eV), or to nonbonding π (−7.74 eV) or HOMO (C=C, π) (−7.92 eV) correspond to BL and UV emissions, respectively. From Figure 6c, the energy level (−3.35 eV) of CB of ZnO QDs can be seen to be slightly higher than that (−3.45 eV) of LUMO (C=C, π*) of ANSA; also, (−7.92 eV) of HOMO (C=C, π) is quite a bit deeper than that (−6.75 eV) of VB of ZnO QDs. This means that ZnO@ANSA hybrid QDs belong to type II core–shell QDs, whereas the previously reported ZnO@GO hybrid QDs are classified as type I core–shell QDs.[35] In type I ZnO@GO hybrid QDs, the energy level of LUMO (−3.09 eV) of outer GO was higher than CB (−3.22 eV) of inner ZnO and thus photoexcited electrons above the LUMO of GO were transferred to CB of ZnO. Afterward,
these electrons were nonradiatively relaxed into shallow donor levels of Zn, and emitted blue luminescence inside ZnO QDs while transitioning to deep acceptor V_{Zn} defect levels. Figure 6d shows the changes of PL intensity of ANSA and ZnO@ANSA and the dispersion of the BL intensity. As $\lambda_{ex}$ increases, the intensity of the BL peak for ANSA monotonously decreases; however, that for ZnO@ANSA increases and reaches a maximum at $\lambda_{ex} = 340$ nm. It then decreases sharply and ceases at values longer than $\lambda_{ex} = 400$ nm. So, the increase of BL intensity in the range of $\lambda_{ex} = 300$–$340$ nm may be attributed to charge transfer both from CB of ZnO QDs to LUMO of ANSA and from the shallow donors of ZnO QDs to nonbonding $\pi^*$-states, which has been frequently observed in inorganic/organic hybrid materials.[25,26] From PLQYs’ measurement, the PLQYs for ZnO QDs is about 30% and slightly decreases to 23% for ZnO@ANSA core–shell QDs. This results from the charge transfer from ZnO to ANSA and well support that ZnO@ANSA is a type II blue emitter. BL for ANSA shows some dispersion in the position of maximum intensity from 450 nm at $\lambda_{ex} = 300$ nm and 428 nm at $\lambda_{ex} = 390$ nm, to 478 nm at $\lambda_{ex} = 420$ nm. This may result from changes of mutual strength at 446 and 472 nm BL as $\lambda_{ex}$ is varied. Unlike ANSA, there is no dispersion in the position of the maximum intensity of the BL peak for ZnO@ANSA.

Figure 7 presents the HOMO and LUMO energy diagram of a single 5-amino-2-naphthalene sulfonic acid (ANSA) molecule including naphthalene, 5 amino-naphthalene, and 2-naphthalene sulfonic acid, as calculated by DFT (Gaussian09 software package). As listed in Table S3, Supporting Information, HOMO and LUMO of naphthalene with 2-aromatic rings consist of solely p$_z$ orbital from the $\pi$-electron; energy gap is estimated at $\approx$4 eV.
When amino group \((\text{NH}_2)\) combines with naphthalene, the compositions of the \(p\) orbitals, composed only of C element, change to \(C:N = 93.26\%:6.74\%\) for LUMO and \(C:N = 82.35\%:17.65\%\) for HOMO. Moreover, the energy levels of HOMO and LUMO in 5-amino naphthalene show shifts of \(\approx 1\) and \(\approx 0.5\) eV, respectively, toward high energy side. On the other hand, when sulfonic acid \((\text{S} = \text{O})_2\text{OH}\) bonds with naphthalene, the elemental compositions of LUMO and HOMO become \(C:S:O = 77.37\%:5.75\%:13.95\%\) and \(77.77\%:0.77\%:3.47\%\), respectively. Different from those of 5-amino naphthalene, the energy levels of LUMO and HOMO move together by about 0.8 eV toward low energy side. As a result, the elemental compositions of LUMO and HOMO become \(C:S:O = 78.29\%:5.75\%:13.95\%\) and \(77.77\%:0.77\%:3.47\%\), respectively. Since O and S are more dominant than N in LUMO and N is contained more strongly than are O and S for HOMO. Moreover, the energy levels of HOMO and LUMO for ANSA become lower and higher, respectively. Different from those of 5-amino naphthalene, the energy levels of \(C:S:O = 75.29\%:5.75\%:13.95\%\) and \(77.77\%:0.77\%:3.47\%\), respectively. Since O and S are more dominant than N in LUMO and N is contained more strongly than are O and S for HOMO.

As shown in EPR spectra of Figure 8a, without illumination of a xenon lamp the wide and broad resonance spectra with linewidth of about 700 Gauss, without any kink or other distinguishable subpeaks and with sharp slope in all ZnO QDs, expanded from \(H = 2000\) G to \(H = 4500\) G and was centered at around \(g = 2.072\), with some ambiguity. Even if the origin of this peak cannot be definitely defined, this kind of unsymmetrical broad peak has been previously reported in several EPR studies. Such peaks are known to be due to oxygen chemically adsorbed on the surface of ZnO \((1010)\) single crystal located between \(g \approx 2.007\) and \(g \approx 2.05\) and ZnO tetrapod nanorods between \(g \approx 2.00\) and \(g \approx 2.05\); or, the broad peak from the range of \(g = 2.0015\) to \(g = 2.0075\) has been known to be attributed to Zn vacancies. Such a broadening of the EPR signal at about \(g = 2.0034\) in nanocrystalline ZnO \((\text{nc} - \text{ZnO})\) thin films synthesized using Zn acetate dihydrate has been known to be produced by excess defects of Zn vacancies in low sol concentration films of 10 wt%. The broadness has been found to be due to strong dipolar–dipolar interaction among randomly oriented defects, as described elsewhere. As the weight percent of sol concentration increases to 15–25 wt%, this broad peak disappears. Compared with one previous report, the concentration of Zn acetate sol in this work was much lower than 10 wt% and thus a broad EPR peak at \(g = 2.072\) seems to be related to \(V_{Zn}^2\) - , with holes localized on oxygen neighbors. The abundance of \(V_{Zn}^2\) - before illumination indicates that the donors for converting \(V_{Zn}^2\) - to \(V_{Zn}^2\) - are not sufficient in ZnO QDs, and thus the ground state of the isolated doubly ionized zinc vacancy \((V_{Zn}^2\) - ) is relatively high in the band gap. The occurrence of a broad EPR signal centered at \(g = 2.072\) confirms the electronic...
energy levels, including the diamagnetic $V_{Zn}^{2-}$ center at around 0.9 eV and paramagnetic $V_{Zn}^{2-}$ center at 0.19 eV above VB in ZnO QDs, as shown in Figure 6c through PL.

On the other hand, when the Xe lamp is used to illuminate the ZnO QDs, as shown in Figure 8b, a sharp EPR signal at $g = 1.96$ newly appears; this is not observed without Xe light illumination. When Xe lamp is off, this resonance peak quickly disappears. The EPR signal at $g = 1.96$, which has sometimes been uncertainly ascribed to unpaired electrons trapped on oxygen vacancies ($V_{O}^{-}$), has been bound to electrons in CB or shallow donor centers of intrinsic ZnO,[69] or to extrinsic impurities of Al, Ga, In, or interstitial H.[70–76] To monitor the variations of the ESR $g = 1.96$ signal with the excitation wavelength, high-pass cutoff filters with varying wavelength of $\lambda_{CF} = 320–530$ nm are inserted (see Figure S4, Supporting Information); narrow window scan results of SDEPR spectra are presented in Figure 9c. It is noteworthy that the intensity of the EPR peak $g = 1.96$ decreases as $\lambda_{CF}$ increases from 320 to 400 nm and is so weak that the change is not measurable at $\lambda_{CF}$ longer than 400 nm. ZnO QDs show a large dependency of the SDEPR signal at $g = 1.96$ intensity on the excitation wavelength ($\lambda_{exc}$) and a threshold wavelength of $\lambda_{exc} = 400$ nm for this to be detected. This is the same trend as that of the GL observed in PL for ZnO QDs, as shown in Figure 4a. In the case of ZnO@ANSA hybrid QDs (Figure 8d–f), the EPR peak $g = 1.960$ disappears irrespective of the light illumination; instead, a peak $g = 2.006$ newly arises, which is consistent with the value of $g = 2.003$ observed in ANSA. The $g$-values of 2.003 and 2.006 are in a similar range of 2.0025–2.0034, which is typical for free radicals of $\pi$-system of two aromatics.[77] It is also indicated that radical defects trapped in the ZnO@ANSA are present. The disappearance of $g = 1.960$ gives strong evidence of electron transfer from the inner ZnO core to the outer ANSA shell. Photoexcited electrons captured in CB or shallow donor ZnO’s are thought to be transferred to LUMO or to O, N, and S-induced defect centers in the ZnO@ANSA hybrid QDs. Unlike that of the ZnO QDs, the intensity of the EPR peak $g = 2.006$ does not change with variations of the excitation wavelength.

Table 1. EPR parameters evaluated from ZnO, ANSA, and ZnO@ANSA core-shell QDs.

| Samples          | Peak-to-peak linewidth $\Delta H_{pp}$ [Gauss] | $g$-Factor | Spin concentrations $N_s$ [spin $g^{-1}$] | spin–spin relaxation time constant $T_2$ [ns] |
|------------------|---------------------------------------------|------------|----------------------------------------|------------------------------------------|
| ZnO QDs          | 688                                         | 2.072      | N/A                                    | 0.3                                      |
| ANSA             | 10.5                                        | 2.003      | N/A                                    | 20                                       |
| ZnO@ANSA QDs     | 530                                         | 2.169      | N/A                                    | 0.39                                     |
| ZnO QDs          | 6.5                                         | 2.0062     | N/A                                    | 32.3                                     |

To extract the homogeneous component, the EPR spectra of ZnO and ZnO@ANSA QDs are analyzed by Voigt fitting with the first derivative of a Lorentzian function convolved with a Gaussian function (see Figure S6, Supporting Information). $\Gamma_G$ (Gaussian FWHM: inhomogeneous) and $\Gamma_L$ (Lorentzian FWHM: homogeneous) are 5.21 and 6.48 G for ZnO QDs, and 2.19 and 10.1 G for ZnO@ANSA hybrid QDs. Therefore, spin–spin relaxation, related to the homogeneous component as expressed in the Equation (6), is estimated at 17.5 ns for ZnO QDs and 11.2 ns for ZnO@ANSA hybrid QDs.

$$T_2 = \frac{2}{\gamma \Gamma_L}$$

where $\gamma$ is the gyromagnetic ratio of electrons.

To further and more precisely extract the correlation between the SDEPR signal and the visible emission, variations of the normalized SDEPR signal area intensity and the GL intensity are plotted together and compared in Figure 9, which GL intensity shows a maximum at $\lambda_{GL} = 360$ nm corresponding to the individual bandgap of $E_g$, then gradually decreases to 68% at 370 nm and 10.8% at 380 nm for ZnO QDs, and then almost disappears at wavelengths longer than 400 nm. When cutoff filters to vary the wavelength of $\lambda_{CF} = 320–530$ nm are inserted, normalized area intensity of EPR signal $g = 1.960$ is reduced by 40% at $\lambda_{CF} = 370$ nm, rapidly decreases to only 5% at $\lambda_{cut-off} = 400$ nm, and then eventually disappears at $\lambda_{CF}$ longer than 400 nm ($\approx 3.1$ eV). It is worthwhile to note that the dependence of the normalized SDEPR area intensity (A) $g = 1.960$ on the excitation wavelength shows a very similar trend to the GL intensity. This result directly implies that the EPR resonance peak $g = 1.960$ is correlated with the GL of ZnO QDs. In consequence, it can be said that this EPR signal $g = 1.960$ can be related to photoexcited electrons captured at defects existing in the conduction band or at shallow donor levels below CB; the GL is the electronic transition.

<ref>Table 1: EPR parameters evaluated from ZnO, ANSA, and ZnO@ANSA core-shell QDs.</ref>
from CB or shallow donors to not oxygen vacancies but Zn vacancy centers.

3. Conclusions

In conclusion, blueish fluorescent type II ZnO@ANSA core-shell QDs were first synthesized by hybridization of ZnO QDs with ANSA. Charge transfer from ZnO to ANSA invokes kinetic deep defects of $V_{Zn}$ but diamagnetic deep defects of $V_{Zn}$. The EPR signal $g = 1.96$ is also found to derive from paramagnetic defects of captured electron at CB or shallow donors of Zn, involving GL, and it is obvious that both have the same threshold excitation energy of 3.1 eV. The estimated long spin–relaxation time ($T_2$) of about 32.5 ns for ZnO QDs at room temperature can be well explained in terms of the strong localization of photoexcited electrons at the defects of ZnO QDs, instead of by thermalization into CB. These inorganic/organic hybrid QDs of ZnO with functionalized polycyclic aromatic hydrocarbon (f-PAH) and well-known saturated polycyclic aromatic hydrocarbon (f-PAH) and well-known fluorescent type II ZnO@ANSA core–shell QDs were thus synthesized by hybridization of ZnO and ANSA. charge transfer from ZnO to ANSA invokes kinetic deep defects of $V_{Zn}$ but diamagnetic deep defects of $V_{Zn}$.

4. Experimental Section

Materials: All reagents were purchased from commercial sources. Zinc acetate (99.99%), tetramethylammonium hydroxide pentahydrate (TMAH, ≥97%), dimethyl sulfoxide (DMSO, ≥99.7%), ethanol (≥99.5%, anhydrous), chlorobenzene (99.8%, anhydrous), and 5-Amino-2-naphthalenesulfonic acid; $H_2NC_10H_6SO_3H$, ≥95%) (ANSA) were purchased from Sigma-Aldrich. Water refers to deionized water (D.I. water).

Synthesis of ZnO QDs: Zn-rich ZnO QDs were prepared via a low-cost solution precipitation process using Zn acetate (Zn(CH$_3$COO)$_2$) and tetramethylammonium hydroxide (TMAH) at high pH. Here, 5 μM TMAH in 10 mL of pure ethanol (solution A) as a reducing agent and 3 μM Zn acetate in 30 mL of DMSO (solution B) as a precursor were dissolved completely at room temperature for 30 min. Solution B was added slowly dropwise into solution A for 1 h to produce ZnO QDs. The ZnO QDs were washed with excess acetone and the resultant ZnO QDs were collected via centrifugation in the solution at 12 000 rpm for 10 min, after which they were ultrasonically dispersed in pure 15 mL ethanol.

Synthesis of ZnO@ANSA Core–Shell QDs: The ANSA (0.15 g) was uniformly dispersed in 40 mL of DMF. The resultant ZnO QDs (0.53 g), as mentioned above, were dissolved in 300 mL of DMF, after which the 5A2NSA solution was added while continually stirring to form a stable precursor. Subsequently, the mixed solution was heated to 130 °C and maintained at that temperature for 3 h to form ZnO@ANSA hybrid QDs. This was subjected to repeated washing with toluene and acetone by centrifugation. The final ZnO@5A2NSA hybrid QDs were obtained after drying the product at 70 °C overnight.

Characterization: Crystalline structures of synthesized ZnO QDs were characterized by XRD as well as HRTEM. The XRD patterns were recorded using an X-ray diffractometer (Rigaku ATX-G) with Cu Kα radiation of wavelength $λ = 1.5406 Å$ in the scan range 2θ = 20°–80°. TEM samples were prepared by dispersing ZnO QDs dry powders in deionized water to form a homogeneous suspension. HRTEM and diffraction pattern analyses were carried out using a FEI Super-Titan (TMB0-300) STEM/TEM/TEM operating at 300 keV. Energy-dispersive X-ray spectroscopy (EDX) was measured using Talsos F2000X (Thermo Fisher) operating at 200 keV. The size distribution of ZnO QDs was analyzed using a Gatan Microscopy Suite Software (Digital Micrograph, Ver. 2.11.1404.0). Fourier transform-infrared (FT-IR) spectroscopy was carried out using a Perkin Elmer Spotlight 400 N FT-NIR Imaging System. UV–vis absorption data were recorded by a PerkinElmer Lambda 18 UV–vis spectrometer with Q5 grade quartz cuvettes. PL and PLE data were recorded by a Hitachi F-7000 fluorescence system with Q5-grade quartz cuvettes. The quantum yield (QY) data were recorded with JASCO FP-8500 Spectrofluorometer using 120 mm integrating sphere (IFL-835) after calibration with the laser ($λ = 365 nm$). The EPR data were taken at room temperature operating in the standard frequency range 8.75–9.65 GHz (X band) at a power of 36 mW with magnetic fields over the range 200–500 mT and with a JOEL FA-200 spectrometer. The latter has a sensitivity of $7 \times 10^{14}$ spins/0.1 mT and a resolution of 2.35 μT or better with 100 kHz magnetic-field modulation. Calculation of the spin concentration and calibration of the magnetic field were carried out with the standard TEMPOL (4-hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl; $C_9H_{18}NO_2$ (M$_{aw} = 172.25$) solution (10$^{-5}$ mol L$^{-1}$ in benzene) of known g-factor ($g = 2.0057$) and the same amounts (80 mg) of each ZnO QD. To investigate change of the EPR signal under illumination, EPR spectra were obtained under 1 Sun illumination (1000 W m$^{-2}$) using a xenon lamp (Figure S4, Supporting Information). The SDEPR spectra were carefully monitored using a band pass filter to cut off the excitation wavelength ($λ_{cc} = 320–530$ nm: cutoff wavelength) (Edmund Industrial Optics) with resolution of ±10 nm.

Calculation of Spin Density:

$$N_s = \frac{A_s(\text{Scan}_s)^2 G_A M_A (g_s)^2 (S + 1)}{A_s(\text{Scan}_s)^2 G_A M_A (g_s)^2 (S + 1)} \frac{[S]}{[S + 1]}$$

where $s$ and $x$ indicate the standard and QD samples, respectively. $A_s$ is area measured under EPR absorption curve, Scan is horizontal scale in Gauss per unit signal, $G$ is a relative gain of signal amplifier, $M$ is modulation amplitude, $g$ is g-factor of EPR, and $S$ is the spin number. Since $\text{Scan}_s = \text{Scan}_x$, $G_A = G_x$, $M = M_x$, $S_x = S_s/2$, $A_s = 14 741$ for ZnO QDs, $A_s = 51 994$, $g_s = 2.0057$, $g_s = 1.960$, ZnO QDs are 20 mg, and $N_s = 1 \mu$m (A 1 μm TEMPOL solution has 6.023 × 10$^{14}$ spins), therefore spin density $N_s$ (spins g$^{-1}$) can be calculated as $N_s = 14 741 \times (2.0057)^2 \times 6.023 \times 10^{14}/(51 994 \times (1.960)/2 \times 10^{-13} = 9.14 \times 10^{15}$ spins g$^{-1}$).

DFT Calculation: The eigenstate energy and orbital contribution for naphthalene, 1-naphthylamine, 1-naphthalenesulfonic acid, ANSA molecules were calculated using Gaussian 09 package. A Becke-style three-parameter exchange and Lee-Yang-Parr correlation hybrid functional were used with a split basis set of 6-311G(d). The molecular structures were fully relaxed to find out total energy minimum, which was checked by vibrational frequency analysis. The convergence condition of the electronic
iteration and root mean square force on atoms were $1.0 \times 10^{-5}$ and $3.0 \times 10^{-4}$ Hartree, respectively. Density of state were simulated through a convolution of Gaussian curve to the calculated eigenstate energy.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

**Keywords**

blue-emissive quantum dots, oxygen vacancy ($V_{O}^{' -}$), spectral-dependent electron paramagnetic resonance, zinc vacancy ($V_{Zn}^{' -}$), ZnO@5-amino-2-naphthalene sulfonic acid core–shell quantum dots

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