

Luminescent Properties of a Water-Soluble Conjugated Polymer Incorporating Graphene-Oxide Quantum Dots

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We report the incorporation of graphene-oxide quantum dots (GOQDs) into films, diluted solutions, and light-emitting diodes (LEDs) as part of a water-soluble derivative of poly(*p*-phenylene vinylene), or PDV.Li, to investigate their impact on the light-emission properties of this model conjugated polymer. Despite the well-known ability of graphene and graphene oxide to quench the photoluminescence of nearby emitters, we find that the addition of GOQDs to diluted solutions of PDV.Li does

not significantly affect the photoluminescence (PL) dynamics of PDV.Li, bringing about only a modest quenching of the PL. However, loading the polymer with GOQDs led to a substantial decrease in the turn-on voltage of LEDs based on GOQD-PDV.Li composites. This effect can be attributed to either the improved morphology of the host polymer, resulting in an increase in the charge mobility, or the enhanced injection through GOQDs near the electrodes.

1. Introduction

Graphene and its chemical derivatives have been attracting huge academic and industrial interest, owing to their potential in a wide range of applications.^[1] Graphene oxide (GO)^[2] is a water-soluble chemical derivative of graphene that is well-known for its scalable synthesis and solution processability.^[2b,c,e,3] GO can be viewed as constituted of a matrix of hexagonally packed sp²- and sp³-hybridized carbon atoms with covalently attached oxygen functional groups. Unlike graphene, which is semimetallic, GO is a photoluminescent insulator with luminescent localized states.^[2c,e] Oxidative cutting of GO results in the formation of so-called GO quantum dots (GOQDs) with typical lateral dimensions of approximately 10–15 nm.^[4] Although GOQDs are chemically similar to GO, they exhibit higher water solubility and typically distinct photoluminescence (PL) characteristics, which occur in the visible to near-IR

range.^[3] These properties of GO and GOQDs make them potentially useful for optoelectronics,^[2d] drug delivery,^[2g] and biomedical sensing.^[5]

Incorporation of GO sheets and GOQDs into polymeric materials enables the exploration of new functionalities arising from the interaction between guest and host materials. For example, use of reduced GO (rGO) as an electron acceptor in bulk heterojunction solar cells has recently been demonstrated.^[6] However, as-prepared GO is essentially hydrophilic and cannot be used directly in blends with most conjugated polymers, which are commonly soluble in organic solvents. Appropriate functionalization of GO is therefore needed to achieve their solubilization in the same organic solvent as the conjugated polymers.^[2c,g,7] The alternative approach that we explore here is to utilize polymers that are soluble in water or polar solvents, such as the precursor to poly(*p*-phenylene vinylene) (PPV)^[8] or derivatives of poly(4,4-diphenylene vinylene) carrying lithium-sulfonated water-solubilizing chains (PDV.Li; for the chemical structure see Figure S1 in the Supporting Information).^[9] The latter polyelectrolytes, for example, have previously been studied as model systems to investigate the potential to prevent aggregation and subsequent PL quenching by "rotaxination", that is, by threading of the conjugated backbones into insulating cyclodextrin rings that act as spacers.^[9b,c] In our previous work, we found that polyethylene oxide (PEO)^[10] wraps around the conjugated polyanionic backbones (as it also does with DNA), thereby mitigating aggregation quenching, and a similar effect is also observed upon substitution of the Li counter cations with cationic species of increasing size.^[11] We considered that the hydrophilic groups of GOQDs might also closely interact with the polar groups of the conjugated polyelectrolytes, as in the case of PEO, and that this effect could also contribute to separate the polymer chains, thus suppressing aggregation and PL quenching. This is particularly interesting, because al-

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though rotaxation is effective at controlling the photophysics of conjugated cores, and even enables ultrabroad gain bands^[12] and fabrication of white-emitting LEDs,^[13] wrapping of the backbones with cyclodextrin macrocycles or amylose linear chains^[14] impairs charge transport, with a concomitant and undesirable increase of the turn-on and operating voltages of light-emitting diodes (LEDs).

Herein, we explore the incorporation of GOQDs into films, diluted solutions, and LEDs based on PDV.Li to investigate their impact on the conjugated polymer optical (and electroluminescent) properties. Although graphene and GO are known to quench the PL from nearby molecules through efficient energy transfer,^[15] we find that the addition of GOQDs to diluted solutions of PDV.Li does not significantly affect the PL dynamics of PDV.Li, bringing about only a modest quenching of the PL. Furthermore, we show that LEDs based on GOQD-PDV.Li composites exhibit significantly reduced turn-on voltages compared to the neat PDV.Li devices.

2. Results and Discussion

Starting our discussion with the morphological and structural properties, we report a tapping-mode atomic force microscopy (AFM) image of GOQDs on a Si/SiO₂ substrate in Figure 1. An

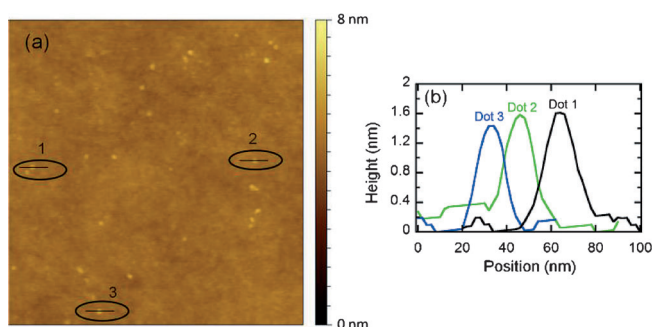


Figure 1. a) Tapping-mode AFM images of GOQDs deposited on a Si/SiO₂ substrate. GOQDs were deposited from a water solution with a concentration of 0.5 mg mL⁻¹ by spin coating. Following the deposition, the sample was annealed at 150 °C in a glove box for 1 h. b) Thickness profile of the selected three GOQDs shown in (a). These are representative of most GOQDs, which are found to be characterized by a height of 1.4 nm and a lateral size of 10–15 nm at FWHM. No tip-deconvolution correction has been applied.

apparently uniform distribution of GOQDs is observed, with lateral sizes between 10 and 15 nm (full-width at half maximum, FWHM,) and thicknesses of approximately 1.4 nm. Such thicknesses correspond to 1–2 layers of GO sheets, in agreement with earlier work. Previously, nano-GO functionalized with polyethylene glycol (PEG), or “PEGylated nano-GO”^[2g] has been reported as a composite in which the PEG chains help to break as-prepared GO sheets (10–300 nm) into smaller flakes with average dimensions of 20 nm.

Absorption and PL spectra of neat PDV.Li and GOQDs in solution (0.05 mg mL⁻¹) are presented in Figures 2a and b. Here, we observe the typical absorption peak of GOQDs at 5.5 eV (225 nm), corresponding to the π - π^* resonant transition. It is

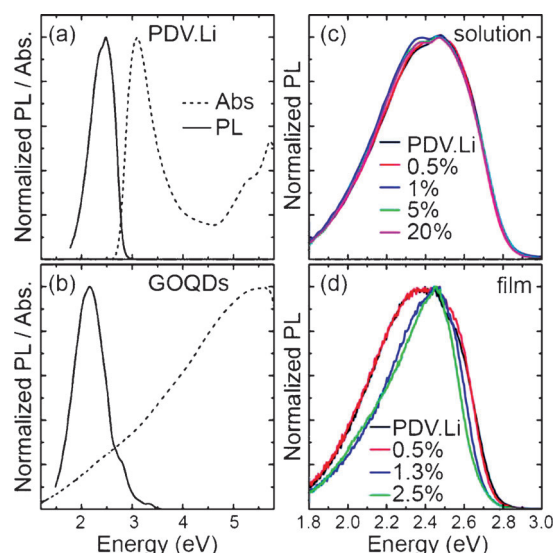


Figure 2. Optical absorption and PL spectra of neat a) PDV.Li and b) GOQDs in solution. PL spectra were collected by using a HeCd laser ($\lambda_{\text{ex}} = 325$ nm) as the excitation source. The PL efficiency of the PDV.Li in solution was $23 \pm 2\%$, whereas that of the GOQDs was less than 1%. c) Normalized PL spectra of PDV.Li:GOQDs blends in solutions with different ratios. d) Normalized PL spectra of PDV.Li:GOQDs in films with different GOQDs loadings. The PL spectra in (c) and (d) were collected by using a pulsed laser diode ($\lambda_{\text{ex}} = 371$ nm) as the excitation source.

worth noting that, unlike GO^[3,16] and graphene quantum dots (GQDs),^[17] the absorption peak at ≈ 4.13 eV (300 nm), which is attributed to the n - π^* transition, is absent in our GOQDs. The PL spectrum of GOQDs peaks at 2.17 eV (572 nm), which is close to the previously reported emission from nano-GO (20 nm)^[2g] and GQDs (1–4 nm).^[17b] Another emission component centered around 2.81 eV (440 nm) is also evident from the emission spectrum. This peak has been previously observed for 5–10 nm GQDs.^[17,18] This blue emission is ascribed to the recombination of electron–hole pairs that are generated within sp^2 cluster domains,^[2c,3] whereas the yellow–red emission (≈ 572 nm) may be associated with the disorder-induced localized states that lie within the π - π^* gap, as recently discussed for GO.^[19]

Figure 2c shows the PL spectra of PDV.Li:GOQDs blends with different weight ratios in aqueous solution (concentration of PDV.Li is kept constant at 0.05 mg mL⁻¹). PDV.Li shows a main PL peak at 2.48 eV (500 nm) with a shoulder at around 2.38 eV (520 nm; Figure 2a). The emission features remain largely unchanged with increasing concentration of GOQDs. The shoulder component around 2.35 eV is, however, slightly enhanced, whereas the main emission peak remains at 2.48 eV. A rearrangement of the PDV.Li vibronic transitions was previously observed in a PDV.K:PEO system as a function of PEO loading,^[11b] although with a concomitant blue shift of both peaks, which we do not observe here.

It is worth noting that the PDV.Li PL quantum efficiency (PLQE) of these solutions is quenched by only $\approx 5\%$ with a GOQD loading of up to 20% (see Table S1 in the Supporting Information for the PLQE as a function of GOQD concentration). Similarly, we do not observe significant changes in the

temporal decay of the luminescence of PDV.Li in the presence of GOQDs or a progressive effect as a function of loading (see Figure S2). This is surprising, because GO has been reported to be an efficient PL quencher,^[5,20] owing to charge/energy transfer. Although some quenching of the PL appears to occur in our system, presumably by the negatively charged surface of GOQDs, it is minor and does not compromise the overall efficiency of the active material. The behavior described above is also markedly different with respect to that observed for the reported conjugated polyelectrolytes (PDV.Li and rotaxinated derivatives), for which either rotaxination, addition of PEO, polyvinyl alcohol (PVA),^[21] or substitution with larger cations induces large increases in the PLQE, blue shifts, and changes in the dynamics temporal decay (e.g. in the weights of excitons vs. aggregate luminescence).^[9b,11,12]

We also investigated the PL of thin films of GOQDs, PDV.Li, and relative blends in different weight ratios, as shown in Figure 2d. The spectra of the neat PDV.Li films and that of the composite with a 0.5% GOQDs loading are essentially identical, whereas higher loadings of GOQDs induce an overall narrowing of the emission, accompanied by a minor blue shift of the peak.

Such a blue shift is most likely attributed to reduced aggregation of PDV.Li, similar to the case of rotaxination or encapsulation by PEO or amylose.^[9b,22] In this case, however, the PLQE does not show any noticeable enhancement (see Table S2). A possible explanation for the blue shift is that positively charged lithium ions mediate a coulombic interaction between the negatively charged GOQDs and the negatively charged anionic polymeric cores, thereby hindering aggregation. Lack of strong PLQE modifications following doping with GOQDs may be explained by competition between two opposing effects, that is, an increase in the PLQE upon suppression of aggregation and PL quenching induced by the GOQDs.

The surface morphology of the films containing different concentrations of GOQDs is shown in Figure 3. The film roughness (R_a) decreases from 2.11 (Figure 3a) to 0.91 nm (Figure 3d) with increasing concentration of GOQDs. This behavior is somewhat similar to the change in polymer packing geometries induced through progressive cyclodextrin encapsulation,

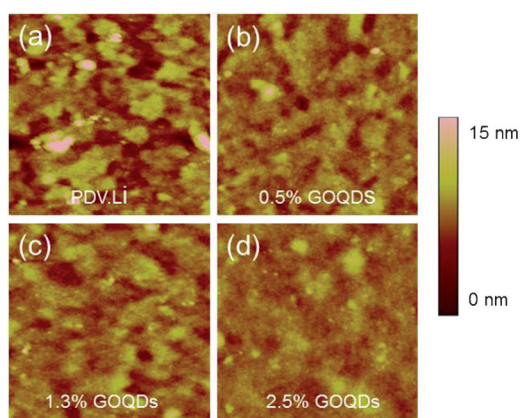


Figure 3. $2 \times 2 \mu\text{m}^2$ AFM images of PDV.Li-GOQDs composites on ITO substrates.

in which the more rigid polymer backbones reduce the roughness of spin-coated films.

To obtain further insight into the properties of such composites, we prepared and characterized the properties of LEDs with the PDV.Li:GOQDs composite film as the emissive layer. Figure 4a shows the electroluminescence (EL) spectra for devi-

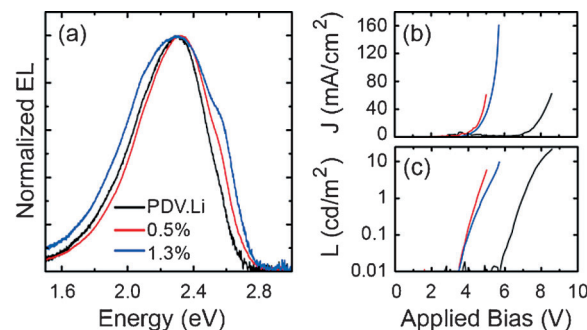


Figure 4. a) Normalized EL of the devices. b) Current density and c) luminance of devices with different loadings of GOQDs.

ces with up to 1.3% GOQD loading. It may be noted that we could not obtain accurate and reproducible results from devices at higher GOQD concentrations. As commonly observed, the EL spectra of the films are red-shifted (by 0.1 to 0.15 eV nm in this particular case, depending on the GOQDs loading) compared to the PL spectra.^[23] The EL spectra for the PDV.Li:GOQDs composites show enhanced peaks/shoulders at 2.08 and 2.55 eV, respectively.

In Figures 4b and c, we show current density and luminance against voltage (J - L - V) characteristics. Interestingly, the device turn-on voltage (measured as the voltage for which the luminance exceeds 0.01 cd m^{-2}) reduces from $\approx 5.8 \text{ V}$ for the neat polymer device to 3.6 V for devices with 0.5 and 1.3% GOQD loadings. Consistently, the current density significantly increases for a fixed voltage as a function of the GOQD loading, thus indicating either improved mobility in the active layer or reduced barriers to charge injection. The external quantum efficiency (EQE) of the blend devices (see 0.5 and 1.3% in Figure S3) is lower compared with the pure PDV.Li device, owing to the aforementioned increase in conductivity of the device, which is not followed by an increase in luminescence. We consider this effect to be caused by a worsening of the charge carrier balance rather than to additional quenching, which the PL experiments above seem to exclude. Despite the low values, it must be noted that there is no EQE drop off with current density and/or GOQDs loading.

3. Conclusions

GOQDs only marginally affect the light-emitting properties of PDV.Li both in solution and in films, inducing a PLQE quenching of approximately 5% in solution followed by small modifications of the PL spectral shape in both cases. More importantly, the GOQDs greatly reduced the turn-on voltage of PDV.Li-based LEDs, either as a result of enhanced charge mobility in

the active layer or of reduced barriers to injection at one or both of the electrodes. We propose that this enhancement, combined with additional device optimization strategies such as introduction of optimized charge transport or blocking layers^[24] as well as electrode work-function engineering,^[25] could be exploited to reduce the operational voltage of organic LEDs, thus improving their operational lifetime^[26] as a result of lower power dissipation on the actual devices.

Experimental Section

GOQDs Synthesis

The GOQDs were synthesized by using GO and a modified Hummers method.^[14,27] After drying, a GO sheet was formed and then thermally reduced at 500 °C in a tube furnace under a gas flow. GOQDs were obtained by subjecting the rGO sheet in a mixture of concentrated H₂SO₄ and HNO₃ to ultrasonication. This process led to re-oxidation and cutting of the rGO sheet into nanometer-sized ensembles. The product was purified by repeated filtration with deionized water. The obtained GOQD water solution was sonicated for 30 min before being used.

Preparation of PDV.Li:GOQD Solutions

Optical studies were carried out on water solutions of PDV.Li (0.05 mg mL⁻¹). Different amount of GOQDs were added to the PDV.Li water solutions, obtaining concentrations of 0.5, 1, 5, and 20% (by weight), thus maintaining the PDV.Li concentration as constant at 0.05 mg mL⁻¹. None of the solutions were filtered to minimize uncertainties in concentration caused by material loss. After adding the GOQDs, the solutions were sonicated for 10 min to ensure good mixing of the two components.

Preparation of PDV.Li:GOQDs Films

Two starting water solutions were prepared, namely **A** and **B**. Solution **A** contained PDV.Li with a concentration of 20 mg mL⁻¹. Solution **B** contained 20 mg mL⁻¹ PDV.Li (as in solution **A**) and 0.5 mg mL⁻¹ GOQDs. Solutions **A** and **B** were then mixed to prepare solutions with different ratios of GOQDs to PDV.Li, namely 0.5, 0.8, and 1.3%, maintaining the PDV.Li concentration as a constant. Therefore, the highest ratio of GOQDs to PDV.Li in a blend was 2.5% by weight (solution **B**). Film deposition was carried out by spin coating to obtain uniform films with a suitable thickness (≈ 100 nm).

Optical Absorption and Photoluminescence Measurements

UV/Vis absorption spectra were obtained with an Agilent 8453 spectrophotometer. PL spectra of GOQD and PDV.Li solutions were excited with a HeCd laser ($\lambda = 325$ nm) and collected with an Andor Newton EMCCD camera coupled to an Andor SHAMROCK 163 spectrograph. Solution PL quantum efficiencies (PLQEs) were measured relative to a quinine sulfate dehydrate in 1.0 N sulfuric acid solution (≈ 10 –5 M, PLQE = 54.6 \pm 5%, NIST standard reference material SRM# 936a, www.nist.gov/srm) by using a time-correlated single photon counting (TCSPC) unit (Edinburgh instruments, F900, time response ≈ 150 ps) and a pulsed laser diode ($\lambda_{\text{ex}} = 371$ nm, pulse width ≈ 40 ps) as the excitation source. The collection wavelength was set at 500 nm.

LED Fabrication

Indium tin oxide (ITO) substrates were ultrasonically cleaned in acetone and isopropanol, followed by O₂ plasma treatment^[28] for 5 min before the PDV.Li:GOQDs water solutions were spin-coated on top of it. Finally, 50 nm calcium and 150 nm aluminum layers were thermally evaporated as the top electrodes. The active layer was about 100 nm thick, as measured by a Dektak surface profilometer. EL spectra were measured with the same setup used for PL measurements. current–luminance–voltage (*J–L–V*) measurements were carried out by using a Keithley 2400 sourcemeter to drive the device and a calibrated silicon photodetector connected to a Keithley 2000 multimeter to detect the luminance.

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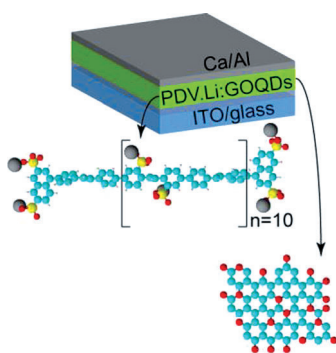
ARTICLES

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 **Luminescent Properties of a Water-Soluble Conjugated Polymer Incorporating Graphene-Oxide Quantum Dots**

 Special Feature



Strange but true: Small quantities of graphene-oxide quantum dots blended in the active layer of polymer light-emitting diodes boost the current density by reducing the turn-on voltage; yet, unexpectedly, they do not decrease the photoluminescence efficiency of the active layer.