

Azobenzene dendronized carbon nanoparticles: the effect of light antenna†

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Fluorescent carbon nanoparticles are grafted with azobenzene dendrons, giving unique dendronized carbon nanoparticles that exhibit an increased quantum yield by as much as ~74% at a low concentration. Such an improvement is attributed to the strong light harvesting capability of grafted azobenzene dendrons that act as "light antenna" to collect photons and the excitons generated then traverse to adjacent central carbon nanoparticles.

Carbon nanoparticles (CNPs) represent a new class of elemental carbon nanomaterial system after fullerenes, carbon nanotubes and graphene. CNPs have aroused the interest of scientists around the world since their discovery by Scrivens *et al.* in 2004.¹ CNPs exhibit strong photoluminescence with high photostability, superior biocompatibility and environmental friendliness,^{2–6} which fuels great expectations for many promising applications, particularly in biomedical,^{7–10} optics,^{11–13} and energy devices.^{14,15} Further, it was observed that a simple surface passivation can play a pivotal role in the overall luminescence characteristic.¹⁶ However, most of the applied surface passivation agents, such as poly-(propionylethylenimine-co-ethylenimine),² polyethylene glycol,¹⁷ mercaptosuccinic acid,¹⁸ serve mainly to remove the surface states, and to improve the solubility and thus processability of CNPs. In this communication, we report a novel surface functionalization of CNPs with azobenzene dendrons. In recent decades, the azobenzene moiety has been a subject of intense interest because of its

cis-trans photoisomerization, high light harvesting and birefringence.^{19–21} Recently, it was shown that nanomaterials functionalized with azobenzene units can exhibit extraordinary optical and electronic properties including efficient charge transfer, enhanced quantum yield, changed electrical field, remarkable photostability and ultrafast kinetics,^{22–24} and can be used for novel applications, such as a light-responsive nanosensor for drug delivery,²⁵ reversible optical information for storage media, optical switches or morphology changes in liquid crystal molecules for sensing, *etc.*^{22,23,26,27}

In this study, we first prepared CNPs in a microwave-assisted chemical reaction from citric acid and urea according to

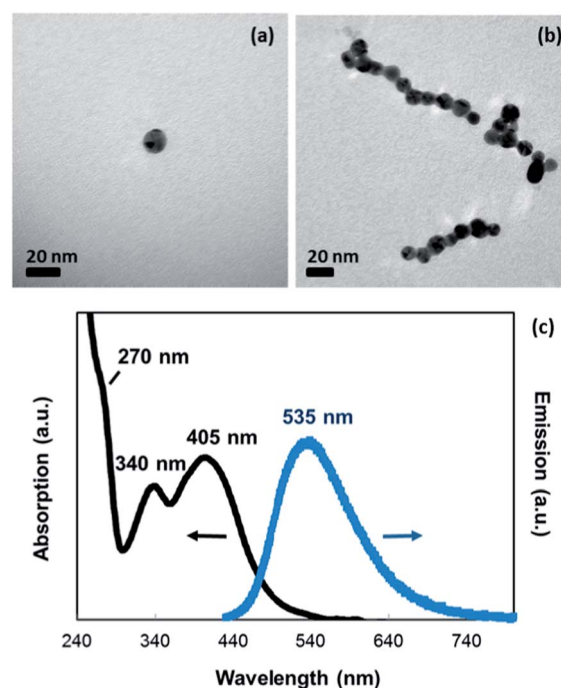


Fig. 1 (a and b) TEM image, and (c) absorption and emission spectra of the prepared CNPs.

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Qu *et al.*²⁸ Fig. 1 shows the TEM image, absorption and emission characteristics of typical prepared CNPs. TEM samples were created by dropping a solution containing the prepared CNPs onto a copper grid. Basically, isolated CNPs can be easily observed (Fig. 1a). For easier imaging of accumulated CNPs in order to provide an overview of their size and distribution, TEM samples were prepared by repeated dropping (Fig. 1b). In both cases, CNPs of ~ 10 nm diameter can be found and they are water soluble with absorption peaks at 270 nm, 340 nm and 405 nm, which are characteristic of an aromatic π system.²⁸ Green emissions from these CNPs can be observed under UV irradiation, which is consistent with the emission spectrum showing a distinct fluorescence maximum at 535 nm. Subsequent X-ray photoelectron spectroscopic (XPS) analysis revealed that there are $-\text{NH}_2$ and $-\text{COOH}$ groups on the CNPs (see ESI, Fig. S1†), which endow the high solubility of CNPs in aqueous solution. On the other hand, a series of *N*-hydroxysuccinimide modified dendritic azobenzene was prepared *via* the Huisgen 1,3-dipolar cycloaddition between azides and alkynes, which is also known as the “click reaction” (Fig. 2, and detailed synthetic procedure for their preparation is included in ESI†). The dendronized CNPs (d-CNPs) were then characterized by UV-vis absorption spectrophotometry and fluorometry. Fig. 3 shows the absorption and emission characteristics of the first-generation, second-generation and third-generation azobenzene dendrons (G1, G2, G3). All dendrons have a strong absorption maximum at around 425 nm. The absorption signal packet actually consists of two absorption bands at 432 nm and 368 nm that can be attributed to the $\pi-\pi^*$ transition in the *trans* isomer and the $n-\pi^*$ transition in the *cis* isomer.²⁹ They have a high absorption coefficient (G1: $4.84 \text{ L g}^{-1} \text{ cm}^{-1}$, G2: $7.82 \text{ L g}^{-1} \text{ cm}^{-1}$, G3: $11.34 \text{ L g}^{-1} \text{ cm}^{-1}$), and thus have a strong light-harvesting capability; however, they do not fluoresce (Fig. 3b).

As *N*-hydroxysuccinimide ester (NHS) is highly reactive towards amine, the dendritic azobenzene was then grafted onto CNPs through the reaction between the dendritic heads and $-\text{NH}_2$ groups on the CNP surface, leading to d-CNPs (ESI†). On the other hand, in order to estimate the effect of surface

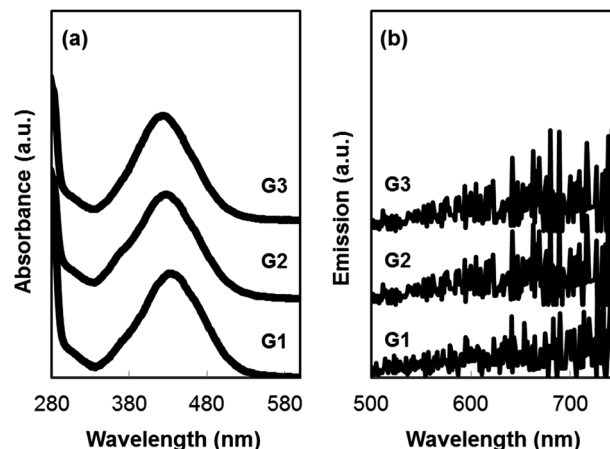


Fig. 3 (a) Absorption and (b) emission characteristics of G1, G2 and G3 azobenzene dendrons.

passivation, some CNPs were treated with CH_3COOH assisted by *N*-hydroxysuccinimide (NHS) and *N*-(3-dimethyl-amino-propyl)-*N'*-ethyl-carbodiimide hydrochloride (EDC). The reaction among CH_3COOH , NHS and EDC enables formation of amine-reactive NHS ester groups that can react smoothly with the $-\text{NH}_2$ groups on the CNP surface, analogous to the coupling between NHS on azobenzene and $-\text{NH}_2$ on the CNP. However, in this case with CH_3COOH , CNPs will be grafted with $\text{CH}_3\text{CO}-$ instead of azobenzene dendrons. For clarity, those CNPs treated with CH_3COOH , NHS and EDC are named a-CNPs. They are an ideal control for investigation of possible surface passivation effect because CNPs can undergo the same type of surface passivation through the coupling between $-\text{NHS}$ and $-\text{NH}_2$. Further, the much smaller size of $\text{CH}_3\text{CO}-\text{NHS}$ can secure an even better accessibility to the CNP surface for passivation than NHS-functionalized azobenzene dendrons. Table 1 lists the quantum yield (QY) of bare CNPs, a-CNPs, and those grafted with G1 (d_{G1}-CNP), G2 (d_{G2}-CNP) and G3 (d_{G3}-CNP) with a number concentration of CNPs at $\sim 1.83 \times 10^{12}$ per mL. The number concentration was calculated by first taking a 10 nm nominal diameter for CNPs (as confirmed by TEM analysis) with a density of graphite at 2.09 g cm^{-3} , which gives a mass of individual CNP of $1.09 \times 10^{-12} \text{ g}$. Then, the number concentration was calculated by dividing the weight of carbon nanoparticles per unit volume used with the estimated mass of an individual carbon nanoparticle. The number concentration given hereafter was also calculated using the same formula.

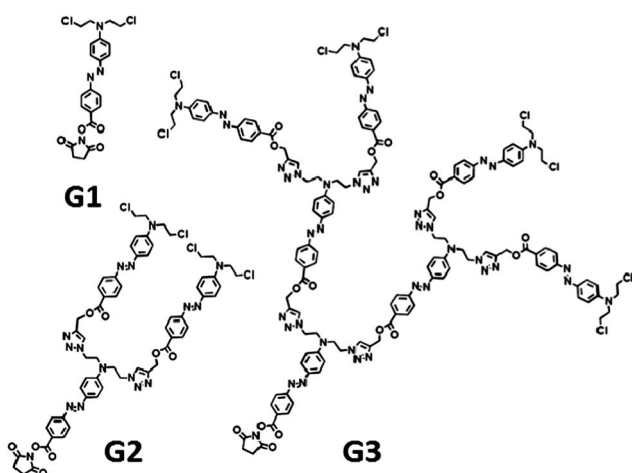


Fig. 2 Chemical structures of first-generation (G1), second-generation (G2) and third-generation (G3) prepared azobenzene dendrons.

Table 1 Quantum yield (QY)^a of treated CNPs

	CNP	a-CNP	d _{G1} -CNP	d _{G2} -CNP	d _{G3} -CNP
QY	12.37%	13.40%	17.41%	17.37%	16.76%
% increase	—	8.3	40.7	39.9	35.5

^a The quantum yield was calculated against the fluorescence of standard quinine sulphate at 337 nm, and was averaged from 3–5 trials. The standard deviations of all QYs measured are <15% of the mean values shown.

The QY measurement reveals an important and interesting finding. Grafting CNPs with azobenzene dendrons can evidently enhance fluorescence and increase QY by as much as 40%. However, it is interesting that surface passivation cannot be the major factor responsible for the substantial fluorescence improvement because the enhancement exhibited by a-CNP is only ~8%. This diminished effect of surface passivation when compared to previous reports^{2,17,18} can be explained by the fact that the urea used for the preparation of CNPs can also serve as a surface passivating agent. Therefore, the QY cannot be improved much by further passivation. Instead, the increased light-harvesting capability translated by the grafted azobenzene dendrons is expected to be a major reason for the increased QY. Since azobenzene dendrons do not fluoresce, emission enhancement through Förster resonance energy transfer (FRET) is excluded because FRET requires a good matching of absorption by energy acceptor (CNP here) with emission by donor (azobenzene here). As judged by the absorption characteristics of CNPs and azobenzene dendrons, they have a very close absorption maximum and substantial overlap. It is reasonably expected that the excitons generated within grafted azobenzene dendrons upon light absorption will have a high chance to transfer to the energy bands of CNPs under thermal fluctuation. It is highly probable because CNPs are known to be both good electron donors and acceptors.³⁰ Consequently, an increased QY can be observed after surface functionalization with the light-harvesting azobenzene dendrons that act as light antenna for the central CNP core. Thus, to further investigate the effects exerted by azobenzene dendrons, the absorption and fluorescence of CNPs dendronized by G1, G2 and G3 were studied in detail (Fig. 4).

As observed in Fig. 4, the absorption at ~420 nm soars upward when compared to that at ~350 nm. This phenomenon can be explained by the enhanced light absorption bestowed by the grafted azobenzene dendrons because of the additional absorption centres on dendritic chains, which have a strong absorption around the same region. Parallel to the increased absorption at ~420 nm, the fluorescence signal component at ~535 nm within the emission packet of CNP increases significantly too. For the emission characteristic, basically two components at 435 and 535 nm can be resolved from the emission packet in both the CNP and d-CNP. Since azobenzene dendrons do not fluoresce themselves (Fig. 3), these two emissions should correspond to two energy band sets of the CNP, and the excitons residing there should be able to easily undergo radiative recombination. As such, the observed increase in absorption at ~420 nm (contributed by azobenzene dendrons) and enhanced emission at ~535 nm (from the energy band set in the CNP) provide further insights into the mechanism of increased QY after dendronization. First, the grafted azobenzene dendrons act as light antenna and harvest photons of ~420 nm. Some of the generated excitons may thermally relax, while many of them can cross to the energy bands in the central CNP, and then to lower energy levels, and eventually radiatively recombine with an emission at ~535 nm (Fig. 5). Therefore, a much enhanced fluorescence as well as the QY can be observed in d-CNPs, where azobenzene dendrons act as effective antenna for light harvesting.

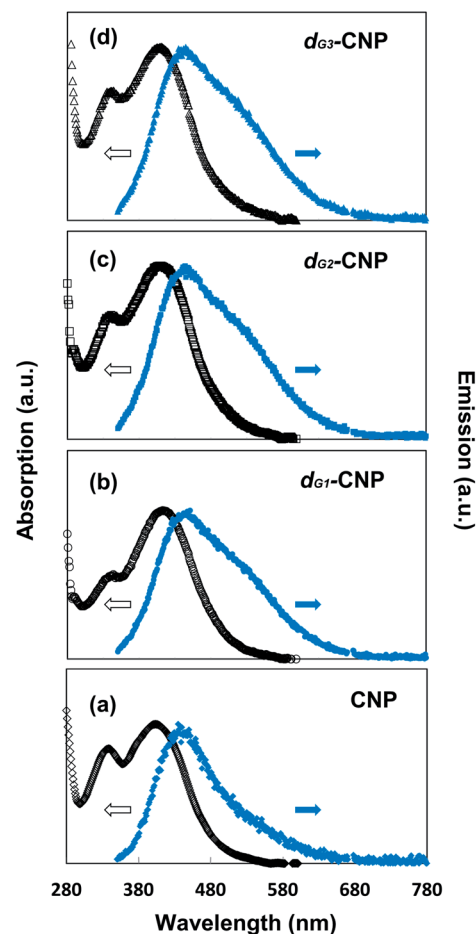


Fig. 4 Absorption and fluorescence spectra of (a) CNP, (b) d_{G1}-CNP, (c) d_{G2}-CNP, and (d) d_{G3}-CNP.

More experiments were performed to study the difference exerted by different generations of azobenzene dendrons. The QY of d-CNPs at different concentrations in number of nanoparticles per milliliter was measured (Fig. 6). Two important findings are noted. First, the QY of the d-CNP shows a very strong concentration dependence, which is not found with the CNP. At a concentration of $\sim 2.2 \times 10^{12}$ per

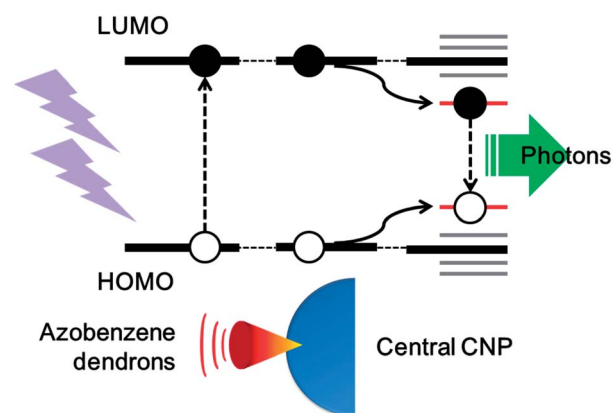


Fig. 5 Mechanism for enhanced emission of d-CNP.

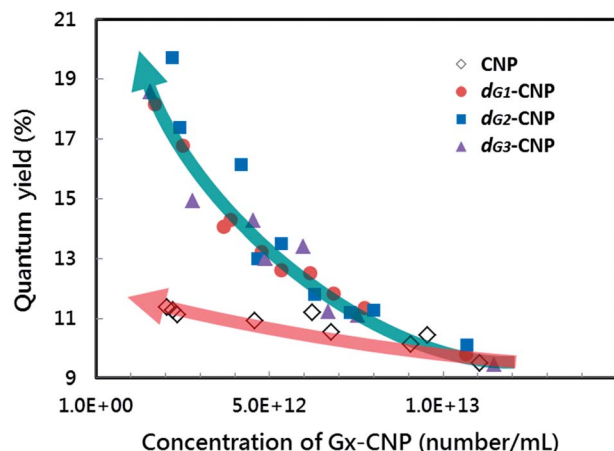


Fig. 6 QY of d-CNPs at different number concentrations. (Each QY is averaged from 3–5 trials. All standard deviations are <15% of the mean value. For clarity, error bars are not plotted.)

mL, the QY of d-CNPs is $\sim 19.7\%$ compared to $\sim 11.3\%$, which represents a substantial increase of $\sim 74\%$. As fluorescent CNPs are known to suffer from aggregation-induced quenching (AIQ),³¹ it is reasonable that emissions from both CNPs and d-CNPs will be gradually quenched towards higher concentrations as observed. However, when the concentration decreases, the QY of d-CNPs rises significantly while that of CNPs just has an incremental increase. It is expected that the azobenzene dendron light antenna are more exposed and thus more accessible to light when the d-CNPs are more diluted. This results in an increased light absorption, and thus an enhanced QY. Second, all dG₁-CNP, dG₂-CNP and dG₃-CNP show the same increasing trend of QY against decreasing concentration. It is an interesting finding because G3 has a higher absorption coefficient than G2, and G2 a higher coefficient than G1. The QY of d-CNP is expected to increase with the number of generations of azobenzene dendrons grafted onto the CNP if the excitons generated within G1, G2 or G3 dendrons can all swiftly traverse to the bands of the central CNP. The observation here thus clearly implies that inter-system crossing of excitons from the azobenzene dendron to the CNP should be distance limited. The travel of excitons should be limited by a length approximately equal to the molecular size of G1, or the travel of excitons is blocked by the triazole groups linking the dendritic arms together in higher generations. The electrical and optoelectronic properties of azobenzene dendrons deserve much more detailed further study.

Nevertheless, it is shown here that the “light antenna” effect exerted by azobenzene dendrons on CNPs is independent of the number of generations. However, CNPs grafted with a different generation of azobenzene dendrons will exhibit different solvent solubility. Although the QY cannot be adjusted by changing the number of dendron generations, control over the latter allows tuning of solubility, thus rendering d-CNPs applicable in more diverse situations where different solvents are involved.

Conclusions

Azobenzene-dendronized CNPs were successfully prepared, and are first reported here. The grafted azobenzene dendrons can act as “light antenna” to harvest light for the central CNP, enhancing the fluorescence characteristics. The QY can be improved by as much as $\sim 74\%$ upon dendronization at a concentration of $\sim 2.2 \times 10^{12}$ per mL. The additional excitons generated within dendrons upon light irradiation are expected to traverse to the energy bands of CNPs through inter-system crossing, and eventually recombine radiatively to give an increased fluorescence. The dendronized CNP shows a distinct concentration dependence, and their QY increases notably with dilution. The present study opens up a new way of surface functionalization of CNPs by photoresponsive azobenzene dendrons. Considering the chemical tunability, versatility and size controllability of azobenzene dendrons, this approach provides a new dimension in passivating CNPs with functional dendrons for unique electrical and optoelectronic properties.

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