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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 which 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. It has aroused interests of scientists worldwide since its discovery by Scrivens et al. in 2004.[1] CNPs exhibit strong photoluminescence with their high photostability, superior biocompatibility and environmental friendliness,[2-6] that fuel substantial excitement and expectation 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 thus processibility of CNPs. In this communication, we report a novel surface functionalization of CNP with azobenzene dendrons. In the last decades, azobenzene moiety has been a subject of intense interest because of its *cis–trans* photoisomerization, highly 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 photo-stability and ultrafast kinetic,[22-24] and can be used for novel application, such as light-responsive nanovalve 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]
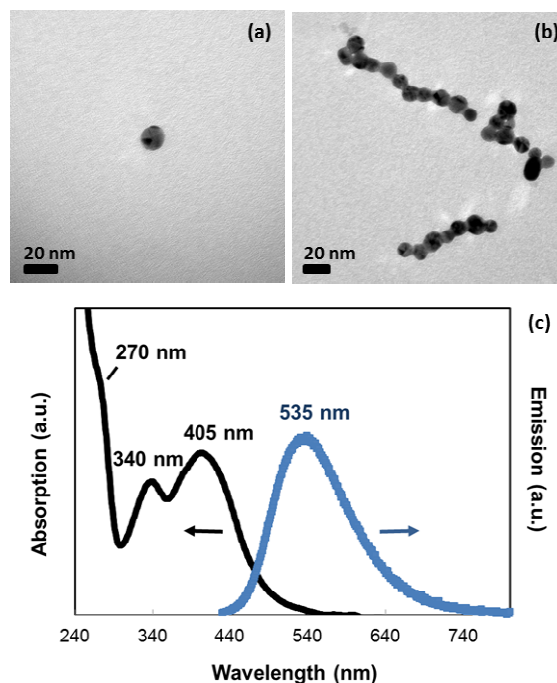

Figure 1. a, b) TEM image, and c) absorption and emission spectra of the prepared CNPs.

In this study, we firstly prepared CNPs from a microwave-assisted chemical reaction from citric acid and urea according to Ref. 28. Figure 1 shows the TEM image, absorption and emission characteristics of typical CNPs prepared. TEM samples were prepared by dropping a solution containing the CNPs prepared onto a copper grid. Basically, isolated CNP can be easily observed (Figure 1a). For easier imaging of accumulated CNPs in order to give an overview of their size and distribution, some TEM samples were prepared by repeated dropping (Figure 1b). In both cases, CNPs of a diameter of ~10 nm can be found and they are water soluble with absorption peaks at 270 nm, 340 nm and 405 nm, that
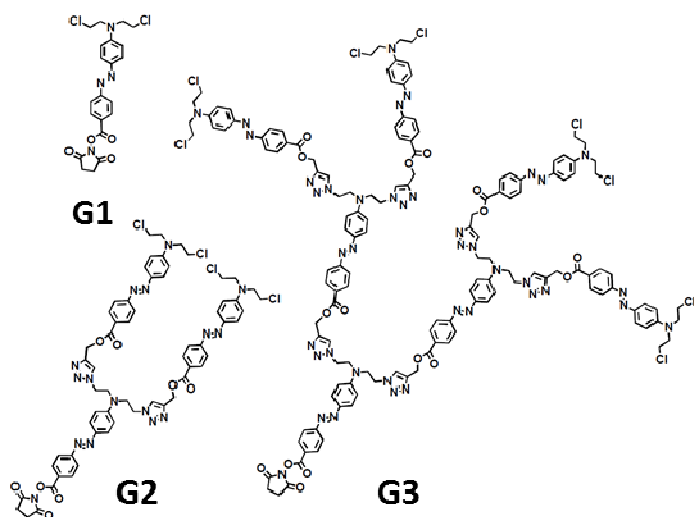
G1

G2   **G3**

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

are characteristics of an aromatic π system.[28]   Green emission from these CNPs can be observed under UV irradiation, that is consistent with the emission spectrum showing a distinct fluorescence maximum at 535 nm. Subsequent X-ray photoelectron spectroscopic (XPS) analysis reveals that there are $-NH_2$ and $-COOH$ groups on the CNPs (see Supporting Information, Figure S1), which endow the high solubility of CNPs in aqueous. On the other hand, a series of *N*-hydroxylsuccinimde modified dendritic azobenzene was prepared via the Huisgen 1,3-dipolar cycloaddition between azides and alkynes, that is also known as the "click reaction" (Figure 2, and detailed synthetic procedure for their preparation is included in Supporting Information). The dendronized CNPs (*d*-CNPs) were then characterized by UV-Vis absorption spectrophotometry and fluorometry.   Figure 3 shows the absorption and emission characteristic 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 π-π* transition in *trans* isomer and the n-π* transition in *cis* isomer.[29] They have a high

absorption coefficient (G1: 4.84 Lg⁻¹cm, G2: 7.82 Lg⁻¹cm, G3: 11.34 Lg⁻¹cm), and thus have a strong light-harvesting capability, however they do not fluoresce (Figure 3b).

As *N*-hydroxylsuccinimde ester (NHS) is highly reactive towards amine, the dendritic azobenzene was then grafted onto CNPs through the reaction between the dendritic heads and $-NH_2$ groups on CNP surface, leading to *d*-CNPs (Supporting Information). On the other hand, in order to estimate the effect of surface passivation, some CNPs were treated with CH_3COOH assisted by *N*-hydroxysuccinimide (NHS) and *N*-(3-dimethyl-aminopropyl)-*N'*-ethyl-carbodiimide hydrochloride (EDC). The reaction between CH_3COOH, NHS and EDC enables formation of amine-reactive NHS ester groups, that can react smoothly with the $-NH_2$ groups on CNP surface, analogous to the coupling between NHS on azobenzene and $-NH_2$ on CNP. However, in this case with CH_3COOH, CNPs will be grafted with CH_3CO- instead of azobenzene dendrons.   For clarity, those CNPs treated with CH_3COOH, NHS and EDC are named as *a*-CNPs. They are an ideal control for investigation of the possible surface passivation effect because CNPs can undergo the same type of surface passivation through the coupling between -NHS and -NH2. Further, the much smaller size of CH_3CO-NHS can secure an even better accessibility to CNP surface for passivation than NHS-functionalized azobenzene dendrons. Table 1 lists the quantum yield (QY) of bare CNPs, a-CNP, and those grafted with G1 (d_{G1}-CNP), G2 (d_{G2}-CNP) and G3 (d_{G3}-CNP) with a number concentration of CNP at ~1.83×10^{12} /mL. The number concentration was calculated by firstly taking a nominal diameter of 10 nm for CNP (as confirmed by TEM analysis) with a density of graphite at 2.09 g/cm³, that give the mass of individual CNP of 1.09×10^{-12} g.   Then, the number concentration was calculated by dividing the weight of carbon nanoparticles per unit volume used with the estimated mass of individual carbon nanoparticle. The number concentration given hereafter was also calculated using the same formula.

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.
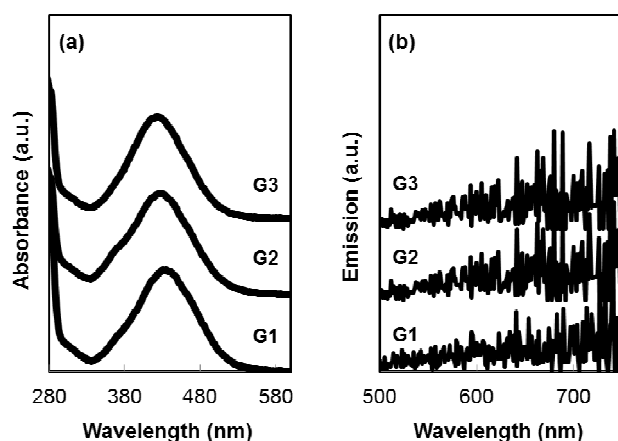
The QY measurement reveals an important and interesting finding. Grafting of CNP with azobenzene dendrons can evidently enhance the fluorescence and increase the QY by as much as 40%. However interestingly, surface passivation cannot be the major factor responsible for the substantial fluorescence improvement 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

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

CNP and azobenzene dendron, they have a very close absorption maximum and have a 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 CNP is known to be both a good electron donor and acceptor.[30] As a result, 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. So as 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 (Figure 4).

It is observed from Figure 4 that the absorption at ~420 nm soars up when compared to the one 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. In 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 CNP and *d*-CNP. Since azobenezene dendrons do not fluoresce themselves (Figure 3), these two emissions should correspond to two energy band sets of CNP, and the excitons residing there should be able to undergo radiative recombination easily. 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 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 central CNP, then to lower energy levels, and eventually radiatively recombine with an emission at ~535 nm (Figure 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.

More experiments were performed to study the difference exerted by different generations of azobenzene dendrons. The QY of *d*-CNPs at different concentration in number of nanoparticles per mL was measured (Figure 6). Two important findings are noted. First, the QY of *d*-CNP shows a very strong concentration-dependence, which is not found from CNP. At a concentration of ~2.2×10^{12}/mL, the QY of *d*-CNP is ~19.7% compared to ~11.3%, that represents a substantial increase of ~74%. As fluorescent CNPs are known to suffer from aggregation-induced quenching (AIQ),[31] it is reasonable that emission from both CNP and *d*-CNP will be gradually quenched towards higher concentration as observed. However, when the concentration decreases, the QY of *d*-CNPs rises significantly while that of CNP just has 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 d_{G1}-CNP, d_{G2}-CNP and d_{G3}-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 than G1. The QY of *d*-CNP is expected to increase with the number of generation of azobenzene dendron grafted onto CNP if the excitons generated within either G1, G2 or G3 dendrons can all swiftly traverse to the bands of central CNP. The observation here thus clearly implies that inter-system crossing of excitons from azobenzene dendron to CNP should be distance-limited. The travel of exciton should be limited by a length approximately equal to the molecular size of G1, or the travel of exciton is blocked by the

triazole groups linking the dendritic arms together in higher generation. This deserves a much detailed further study on the electrical and optoelectronic properties of azobenzene dendrons.
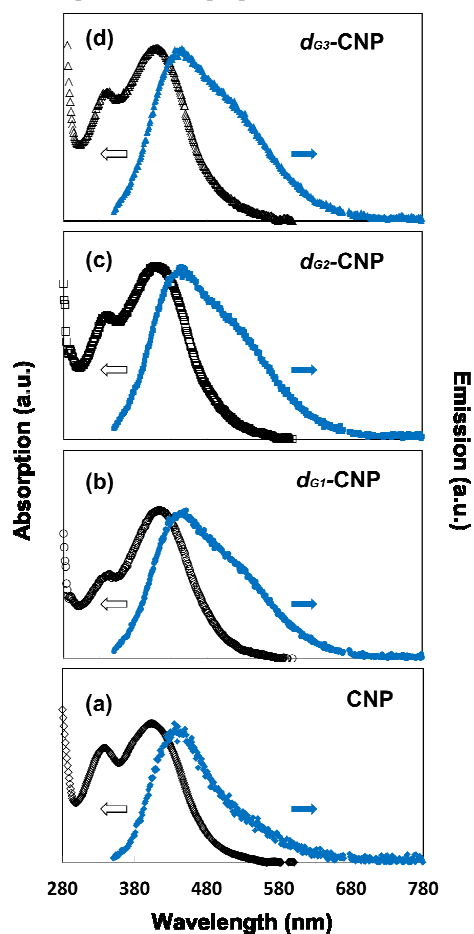

Figure 4. Absorption and fluorescence spectra of a) CNP, b) d_{G1}-CNP, c) d_{G2}-CNP, and d) d_{G3}-CNP.
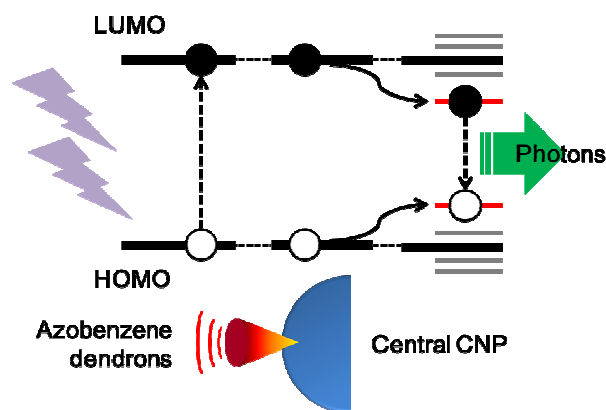

Figure 5. Mechanism for enhanced emission of *d*-CNP.

Nevertheless, it is shown here that the "light antenna" effect exerted by azobenzene dendrons on CNP is independent of the number of generation. However, CNP grafted with different generation of azobenzene dendrons will exhibit different solvent solubility. Although the QY cannot be adjusted by changing the

number of generation of dendrons, the control over the latter allow tuning of solubility, thus rendering *d*-CNP applicable in more diverse situations where different solvents are involved.
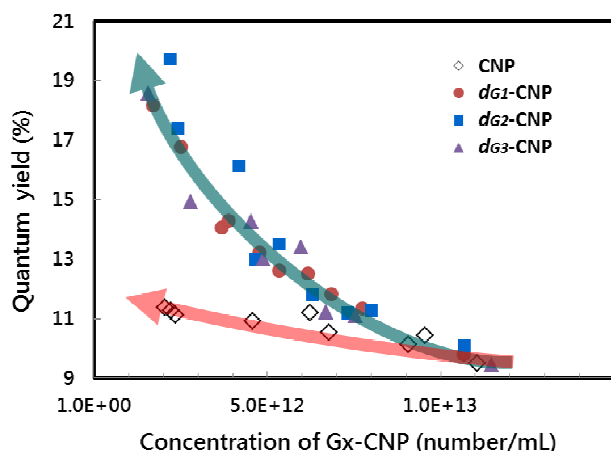

Figure 6. QY of *d*-CNPs at different number concentration. (Each QY is averaged from 3-5 trials. All standard deviation is <15% of the mean value. For clarity, error bars are not plotted.)

Conclusions

Azobenzene endronized CNPs were successfully prepared, and are first reported here. The grafted azobenzene dendrons can act as "light antenna" to harvest light for central CNP, enhancing the fluorescence characteristic. The QY can be improved by as much as ~74% upon dendronization at a concentration ~2.2×10^{12}/mL. The additional excitons generated within dendrons upon light irradiation are expected to traverse to the energy bands of CNP 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 CNP by photoresponsive azobenzene dendrons. Considering the chemical tunability, versatility and size controllability of azobenzene dendrons, this approach provides a new dimension in passivating CNP with functional dendrons for unique electrical and optoelectronic properties.

Notes and references

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