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COMMUNICATION

Self-Assembly Facilitated Visible Light-Driven Generation of Carbon Dots

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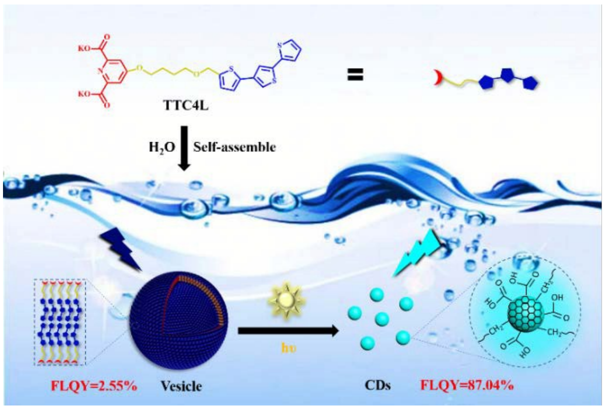
Carbon dots (CDs) with an absolute fluorescence quantum yield of 87% are facilely prepared via mild visible light irradiation of self-assembled terthiophene amphiphile TTC4L in aqueous solution. Visible light irradiation of TTC4L triggers the production of superoxide radical in water which oxidizes the closely packed terthiophene group into carbon dots. Our result reveals that the close and ordered molecular arrangement in molecular self-assembly may act as important precursor for the generation of single molecule like carbon dots, which paves the way for fabrication of CDs of high quality.

Last decades have witnessed the rapid development of molecular self-assemblies owing to their potent application in fabrication of advanced materials, [1-4] especially various smart materials that are responsive to external stimulus, such as light, temperature, pH, etc.[5-7] Besides the responsiveness of molecular self-assemblies, the ordered molecular arrangement is also very useful in material science, such as creating conductive materials,[8] chiral self-assembled structures,[9] and various supramolecular polymers.[10, 11] However, so far, the advantage of ordered molecular arrangement in molecular self-assemblies has been seldom exploited in preparation of carbon dots (CDs).

As a prospective member of nanomaterials, CDs have attracted intensive attention in the field of solar energy conversion,[12-14] bio-imaging,[15, 16] as well as chemical sensing[17, 18] owing to their stable photoluminescence (PL), low cytotoxicity, and excellent biocompatibility. They are ultrasmall fragments of carbon materials with tunable degree of carbonization, which are usually fabricated from carbon soot, graphite or carbon nanotubes via arc discharge,[19] laser ablation,[20] or electrochemical oxidation.[21] Molecular precursors are also widely employed to obtain CDs, where small molecules are treated with hydrothermal[22] or solvothermal[23] cutting strategies, or subjected to microwave pyrolysis,[24] which finally results in nanometer sized carbon materials.

In this work, we show that molecular self-assembly can facilitate generation of CDs under visible light irradiation. Different from the literature methods that require high voltage, temperature, strong acids, or involve the use of special equipment, visible light irradiation of the vesicular self-assembly of a terthiophene amphiphile TTC4L in water can generate CDs with an absolute fluorescence quantum yield up to 87%. Mechanism study shows that photo induced generation of superoxide radicals ($O_2^{\bullet-}$) triggered the carbonization of the terthiophene moiety, which finally leads to generation of CDs. This work for the first time reports the advantage of using molecular self-assembly as the precursors for the fabrication of carbon dots, and the possibility to generate dots with visible light (Scheme 1).

TTC4L was synthesized in our lab,[25] which is an amphiphile with a terthiophene group in the hydrophobic tail tethered to a hydrophilic chelidamic acid head via an oxyl-butyl chain (Scheme. 1). This molecule is able to self-assemble into vesicles in water, and the size of the TTC4L vesicles is concentration dependent.[25] In the present study, vesicles with diameter of 60-90 nm are formed in the 50 µM TTC4L aqueous



Scheme 1. Illustration for the formation of TTC4L-CDs.

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solution (Fig. 1a). The vesicular suspension of TTC4L displays blue emission (Fig. 1b, black line) at 435 nm. However, the fluorescence shifts to 460 nm and keeps increasing (Fig. 1b) upon irradiation with a daylight lamp (25 mW cm^{-2}). After 16 hours, the fluorescence reaches maximum, which is about 5 folds of the original intensity, and the absolute FLQY amounts as high as to 87%. Meanwhile, the UV absorbance of TTC4L decreases (Fig. S1). ^{1}H NMR measurements reveal the disappearance of signals corresponding to the terthiophene group, indicating that TTC4L has undergone photochemical reaction (Fig. S2). TEM observation manifests the formation of small nanoparticles with average diameters of 2.7 nm ± 0.4 nm (Fig. 1c, lower inset). A lattice spacing of 0.32 nm, manifest the distance of the <002> facet of graphitic carbon,[26, 27] can be obtained with high resolution TEM (Fig. 1c, upper inset), indicating the formation of carbon dots (denoted as TTC4L-CDs). AFM measurement shows the average topographic height of the obtained carbon dots are about 1.6 nm ± 0.3 nm (Fig. S3). Obviously, the ultra-high fluorescence quantum yield is from the light generated carbon dots. Fig. 1d reveals that the TTC4L-CDs display a single exponential fluorescence lifetime of 2.5 ns, which is significantly different from the two lifetimes observed for the original TTC4L vesicles (Fig. 1d and Tab.S1)

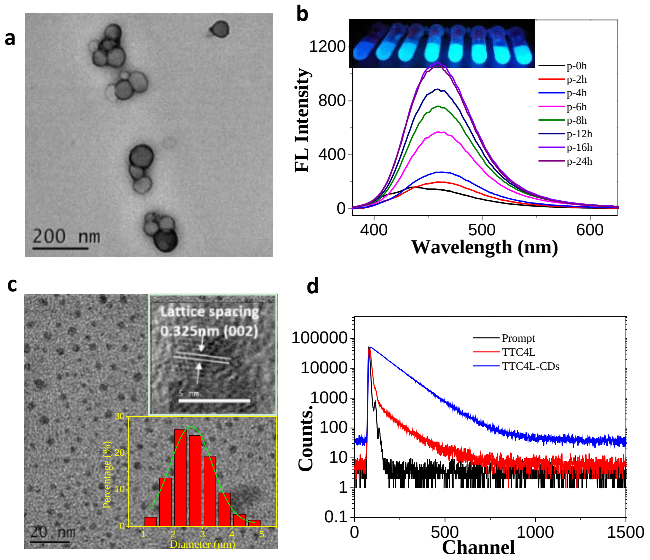

Figure 1. **a)** TEM image of vesicles formed in 50 μM TTC4L. **b)** Fluorescence spectra of 50 μM TTC4L aqueous solution irradiated by a daylight lamp (25mW cm^{-2}) at different times. Inset: Photos of the solution at different irradiation time under 365 UV (from left to right). **c)** TEM image of the CDs (upper inset: high resolution image of the CDs; lower inset: size distribution of CDs). **d)** Fluorescence lifetime of TTC4L and the CDs

The FLQY is usually closely related to the composition and surface groups of CDs[28,29]. X-ray photoelectron spectroscopy (XPS) results (Fig. 2a) indicate that the CDs are mainly composed of carbon and oxygen, with tiny amount of nitrogen and sulphur. It is worth noting that the peak intensity of nitrogen and sulphur in the original TTC4L solution is much stronger than that in the irradiated sample (Supplementary Fig. S4), suggesting the nitrogen and sulphur has gone away from the CDs after light-irradiation. XPS measurement for samples at different irradiating stages(Fig. S5) reveal that the content of original S_{2p} at 163.9 eV and N_{1s} at 399.0 eV of TTC4L decreases with increasing the irradiation time. Meanwhile, a new peak at 168.2 eV (S element in sulfur dioxide) for S_{2p} and a new peak at 401.1 eV (N element in ammonium compound) for N_{1s} occur, suggesting a progressive photo oxidation process of TTC4L. The high-resolution XPS for the final purified TTC4L-CDs can be decomposed into 3 main peaks from different binding state of C_{1s} electrons (Fig. 2b). The one at 284.5 eV can be assigned to the graphitic skeleton (sp^{2} C-C), while the one at 285.5 eV indicates the presence of C-O bond and the C-C single bond, and the peak at 288.0 eV signalizes C=O bond.

The surface state of the TTC4L-CDs was further examined with Raman and FT-IR measurements. The Raman spectrum reveals that the CDs display D and G bands at 1365 and 1570 cm^{-1} respectively (Fig. 2c), which are characteristics of carbon materials. The relative intensity ratio of the D-band and the crystalline G-band (I_D/I_G) is about 0.9, which is a very large value indicating the presence of considerable defects[30,31]. Furthermore, FT-IR spectra (Fig. 2d) manifest the nearly vanishing of the skeletal vibration of the pyridine ring at 1370 cm^{-1}, the C-O-C asymmetric and symmetric stretching vibration at 1100 and 1040 cm^{-1}, and the out-of-plane vibration of aromatic rings at 800 cm^{-1} in the TTC4L-CDs. However, the symmetric and asymmetric stretching vibrations of C=O, around 1409 cm^{-1} and 1565 cm^{-1} still remain there, but the separation between the symmetric and asymmetric viberation decreases by about 100 cm^{-1}, suggesting the environment of the C=O has changed drastically. Meanwhile, a broad vibrational band characteristic of hydrogen bond is observed at 3410 cm^{-1}. These IR features suggest the presence of –COOH groups on the surface of CDs. Indeed, the CDs display reversible pH dependent fluorescence. The fluorescence decreases as the pH decreases, probably due to the hydrogen bonding between the CDs (Supplementary Fig. S6). Specially, the asymmetric and symmetric vibration for -CH$_2$- are also observed at 2921 cm^{-1} and 2850 cm^{-1}, indicating the hydrophobic carbon chain of TTC4L is probably attached to the surface of the CDs, too. It is possible that both the -COOH groups and the pending alkyl chains are beneficial for the high FLQY of the TTC4L-CDs through a surface passivation mechanism[20,28,29].

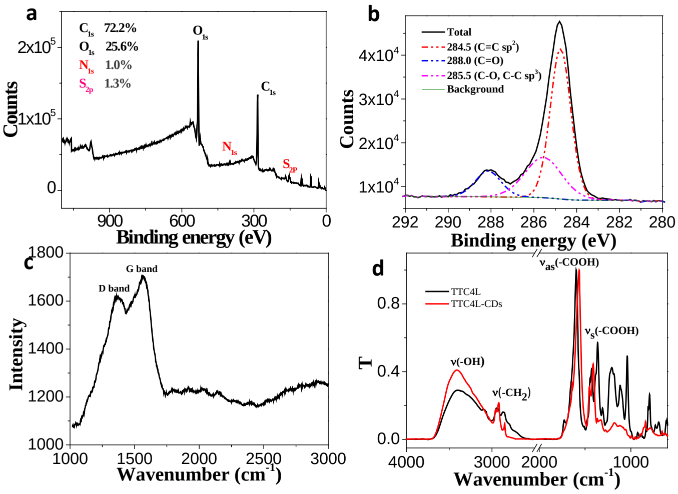

Figure 2. Surface-state characterizations of TTC4L-CDs. **a)** XPS spectrum of TTC4L-CDs. **b)** High-resolution of C1s of XPS spectrum. **c)** Raman spectrum of TTC4L-CDs. **d)** FT-IR spectrum of TTC4L-CDs.

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Unlike most CDs displaying excitation dependent emission[32,33], the emission of the TTC4L-CDs is excitation-independent. As the excitation wavelength altered from 254 nm to 380 nm, the maximum emission wavelength remains constant (Supplementary Fig. S7a), suggesting the emission is originated from defects, rather from band-gap[20,34]. This is in line with the large I_D/I_G value obtained in Raman measurement (Fig. 2c). The defect facilitated emission of the TTC4L-CDs has a narrow full width at half-maximum (FWHM) of only 70 nm (Supplementary Fig. S7b), which is narrower than most of the FWHMs of >100 nm for other CDs[31]. In combination with the single exponential decay of the fluorescence lifetime, we infer that single molecule-like CDs have been generated with light in this work.

Excitingly, the single molecule-like CDs display two-photo fluorescence properties. Fig. 3a reveals that upon exposure to a near-infrared (NIR) femtosecond laser of 730 nm, emission of the TTC4L-CDs occurs as well. With the logarithmic coordinate, the linear slope is 1.89 which describes a clear quadratic relationship between the excitation laser power and the fluorescence intensity (Fig. 3b), confirming that excitation with two NIR photons is responsible for the fluorescence of the CDs[35].

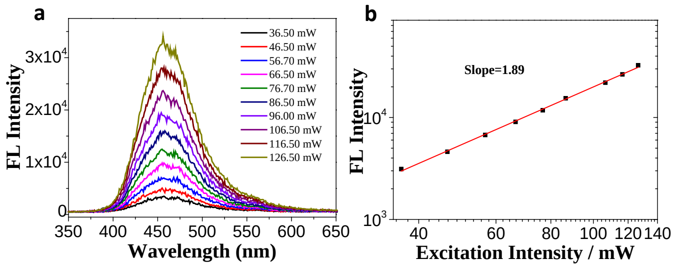

Figure 3. a) Two photon spectra of TTC4L-CDs at different laser excitation intensities of 730nm femtosecond pulse laser. **b)** Relationship between the two-photon emission intensity and laser excitation intensity.

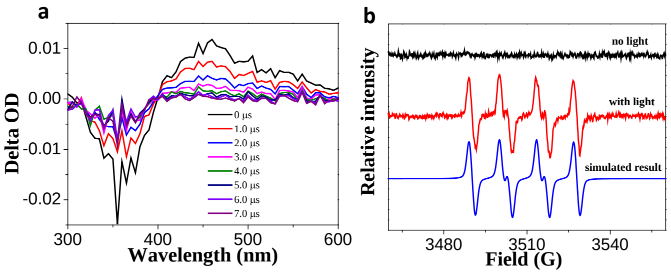

Figure 4. a) Time-resolved transient spectra of TTC4L aqueous solution under 355nm pump light. **b)** Electron paramagnetic resonance spectra of TTC4L aqueous solution by adding BMPO as radical trap agent.

To gain more insight into the formation mechanism of TTC4L-CDs, time-resolved transient absorption (TRTA) spectroscopy was employed to study the intermediate species generated in the photo-irradiation process. The characteristic peak of terthiophene group at triplet state (^{3}TTC4L*)[36] locating at 452 nm was observed (Fig. 4a). The lifetime of ^{3}TTC4L* is about 2.12 μs (Supplementary Fig. S8). This means that the excited triplet TTC4L (^{3}TTC4L*) may have sufficient lifetime to transfer its energy to triplet oxygen to generate ROS. Indeed, as the TTC4L aqueous solution was exposed to light, a typical electron paramagnetic resonance (EPR) signal (Fig. 4b, red line), was observed using BMPO as the radical trap. The simulated result (Fig. 4b, blue line) of EPR signal was quite consistent with the $O_2^{\bullet-}$ signal. Control experiments suggest that no EPR signal can be observed in the TTC4L aqueous system without exposure to light (Fig. 4b, black line), indicating $O_2^{\bullet-}$ is generated by irradiating the TTC4L aqueous system with visible light. The production of $O_2^{\bullet-}$ is very crucial in the visible light generated CDs. As a proof of this argument, when the reactive $O_2^{\bullet-}$ was consumed by degradation of organic dyes, such as rhodamine B, the fluorescence of TTC4L only increases slightly, (Supplementary Fig. S9), confirming the important role of $O_2^{\bullet-}$ in the formation of CDs.

The self-assembling ability of TTC4L is very crucial in the light triggered generation of CDs. Upon dissolving TTC4L in a good solvent such as ethanol, the fluorescence only slowly increased by 1fold after 24 hours irradiation (Supplementary Fig. S10). Furthermore, as the self-assembling ability is enhanced by extending the hydrocarbon chain tethering the coordinating head and the terthiophene group from 4 -CH_2- (TTC4L) to 8 -CH_2- (TTC8L, Fig. 5a), the CDs can be generated even faster. Fig. 5b shows the UV-vis spectra of TTC4L and TTC8L aqueous solution, the stronger aggregated ability of TTC8L than TTC4L lead to the increase of turbidity. In Fig.5c and Supplementary Fig. S11 we show that the fluorescence reaches maximum within 12 hours in the TTC8L system, whereas it takes 16 hours in the TTC4L system. Different from the 60-90 nm vesicles formed by TTC4L, TEM observation reveals the formation of hexagonal structure of 2400 nm long and 500 nm wide in the TTC8L system (Supplementary Fig. S12a). However, the size and emission of the CDs obtained in the TTC8L system is the same as that in the TTC4L system (Supplementary Fig. S12b), indicating the size and morphology of the self-assembled structure does not impact the final properties of the CDs. Last but not the least, the amphiphilic structure of TTC4L is important in the CDs formation. Control experiments suggest that no CDs are formed when simply disperse terthiophene (TT) in water with the same irradiation condition. Although it is insoluble and forms 'aggregates', no obvious fluorescence enhancement was observed (Supplementary Fig. S12). It is possible that self-assembly allows facile diffusion of oxygen into the terthiophene arrays which triggers the carbonization of the TTC4L molecules.

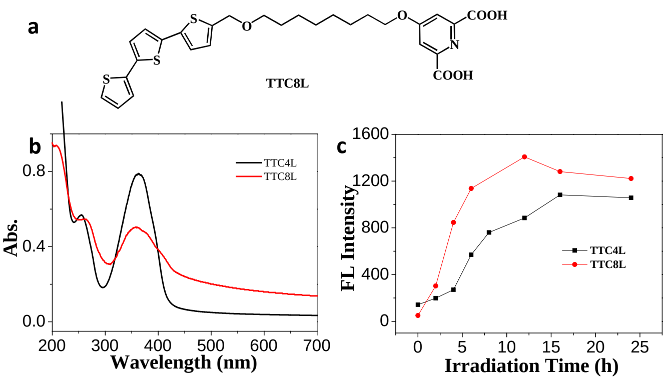

Figure 5. a) Chemical structure of TTC8L. **b)** UV-vis spectra of TTC4L and TTC8L aqueous solution. **c)** Fluorescence intensity of TTC4L and TTC8L aqueous solution with increase of light irradiation time, respectively.

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In summary, we report in this work the first case of visible light generated carbon dots in the molecular self-assembly of a terthiophene amphiphile TTC4L. The resultant CDs display narrow size distribution which endows the CDs with excitation-independent emission and two-photon emission. The absolute fluorescence quantum yield of these CDs can be as high as ca. 87% which is probably owing to the presence of alkyl chains and COOH groups on the surface as a result of the mild photoreaction condition. Mechanism study shows that visible light irradiation facilitates the formation of the long-lived TTC4L triplets, which transfer its energy to oxygen to produce $O_2^{\cdot-}$. The reactive $O_2^{\cdot-}$ radical triggers the carbonization of the terthiophene skeleton in the self-assembly of TTC4L. Although the details for the carbonization is still not clear, we believe that the pre self-assembly of TTC4L is very crucial in the CD formation since it allows the terthiophene groups arrange in sufficient vicinity and order which allows facile generation of C-C bonds. In a word, the present visible light driven strategy provides a new method to prepared high quality CDs, which are promising for myriad applications, such as solar energy conversion, bioimaging, *etc*.

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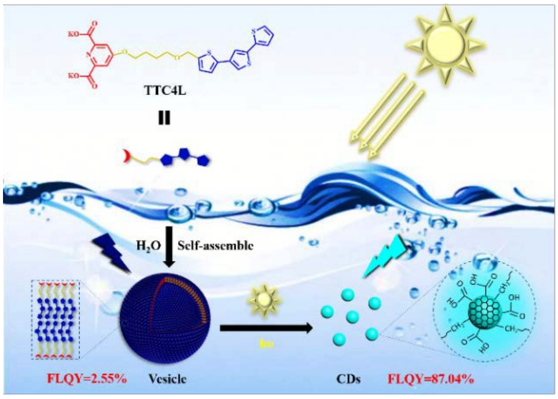

Molecular self-assembly may facilitate visible light generation of carbon dots.