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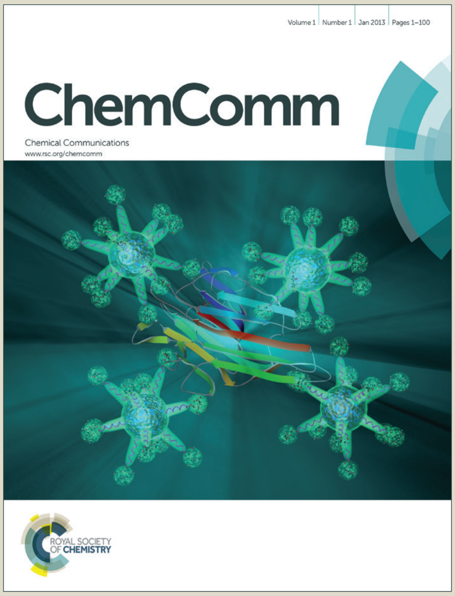

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ARTICLE TYPE

Uncovering a broad class of fluorescent amine-containing compounds by heat treatment

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Amine-containing compounds including polymers, oligomers and small molecules, without conventional fluorophores, are found to emit strong visible fluorescence after a one-step heat treatment. Furthermore, our results first demonstrate that not only tertiary amine groups but also primary and secondary ones can act as fluorescent moieties.

New fluorescent materials with special photo- and/or bio-active features are very attractive for both scientific and applicative reasons. For fluorescent organic compounds, existence of some units with large π-conjugated systems and rigid planar structures is a necessary prerequisite according to classical theory. However, in recent years, strong blue fluorescence from several types of amine-containing polymers without conventional fluorophores was observed, for example, poly(amido amines) (PAMAM),[1,2] polyethylenimine,[3] poly(amino esters),[4] polyurea dendrimer,[5] which have been successfully applied in biological imaging.[5,6] Obviously, the photoluminescence mechanism and properties of amine-containing compounds are quite different from that of the current fluorescent materials; and amine groups are thought to be responsible for the fluorescent emission, owing to the lone-pair electrons on their nitrogen atom.[7] Importantly, Amine-containing compounds are expected to be good candidates for optical and biological materials, because of their outstanding features such as high polarity, biocompatibility and water-solubility relative to conventional chromophores.

To date, research works in this field have several questions. Firstly, although fluorescence emitted from tertiary amine has been extensively studied, the fluorescence from primary and secondary amines is seldom observed, which has been explained in terms of loss of the hydrogen atom via predissociation.[8] Secondly, as mentioned above, studies on fluorescent amine-containing polymers have been reported by many groups; however, there is only a few works on amine-containing small molecules,[7] due to their weak emission in the visible spectral region. Thirdly, there is no reliable and facile method to fabricate fluorescent amine-containing compounds; although some methods such as acidification[1a], oxidation[1b] and synchrotron radiation[3c] have been proposed, these methods are cumbersome and only effective in the cases of amine-containing polymers.

Herein, we first present a one-step heat strategy with outstanding characteristics of versatility, rapidity and facility to obtain fluorescent amine-containing compounds. In a heating process, fluorescent peaks of amine-containing compounds shift gradually from ultraviolet spectral region to visible one. Our experimental results demonstrate two important features: (a) many kinds of amine-containing compounds such as small molecules, oligomers and polymers are found to emit strong fluorescence after heat treatment; and (b) not only tertiary amine but also primary or secondary amine can act as fluorescent moieties. Hence, a broad class of fluorescent amine-containing compounds without any conjugated unit is revealed.

Hyperbranched (HP) -PAMAM was selected to elucidate the fluorescent variations in the process of heat treatment. The experimental details for the synthesis of HP-PAMAM are available in the ESI. † Upon heating at 90 ℃ under ambient condition, colourless pristine HP-PAMAM gradually turned pale yellow and could emit luminescence. Fig. 1 displays the contour plots of excitation-emission matrices (EEMs) measured at different times in the heating process. A gradual increasing of red shift and intensity of fluorescent emission was observed. This variation is likely a consequence of formation of a new N→O chromophore,[7] as a result of oxidation by oxygen in air.[2b] This suggestion is supported by IR spectra (Fig. S1, ESI†), in which characteristic N→O absorption bands are clearly observed after heat treatment.[8b] In a contrast test, a sample with protection by bubbling argon gas exhibited weak fluorescence after same treatment of heating. Our previous work demonstrated that interaction between fluorescent amine centres took place when they got close enough at high concentration, which resulted in enhanced intensity and red shift of fluorescent peak.[9] Hence, it can be speculated that the increasing concentration of oxidized amine groups in the heating process leads to the red shift and higher intensity. This explanation is also confirmed by diluting a fluorescent amine-containing sample, in which the red shift of maximum wavelength position in heating process is reversed (Fig. S2, ESI†).

Furthermore, the results of excited state lifetime demonstrated that there were three discrete fluorescence lifetimes (Table S1, ESI†), which implies the existing of at least three fluorescent species. In addition, based on the data of gel permeation chromatography (Fig. S3, ESI†), it can be

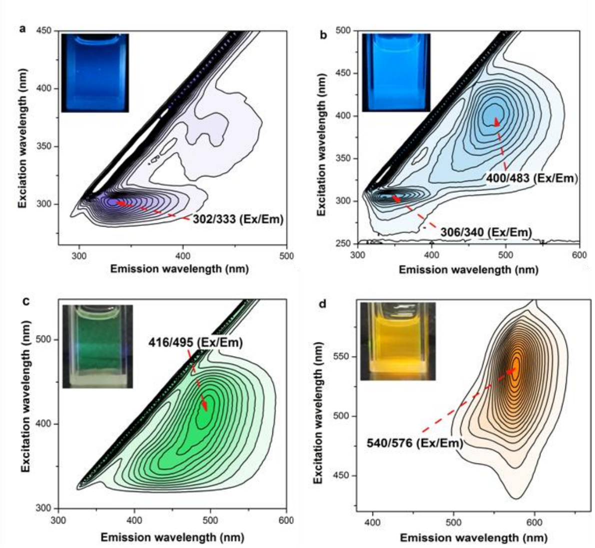

Fig. 1 Contour plot for the fluorescent EEMs of HP-PAMAM measured in the heating process: a) 0, b) 4, c) 12 and d) 18 hr, respectively. Red arrows indicate the position of fluorescent peaks. Inset in a–d, Photographs of corresponding samples under irradiation of their maximum excitation wavelength, respectively.

assumed that the photoluminescence originates from the polymer, rather than its fragments of structure breakdown, although a change of molecular weight distribution of HP-PAMAM in the heating process was observed.

On the other hand, it is obvious that the one-step heat strategy is facile to achieve strong fluorescence in the visible spectral region. In contrast, by means of previously reported methods (i.e. acidification or oxidation), preparation of fluorescent amine-containing polymers is cumbersome and time-consuming, which has been regarded as an obstacle to practical applications. For example, by using oxidation method, it took 20 days to obtain fluorescent amine-containing polymers at below 35 °C under continuous stirring.[8b]

To further explore the temperature effect, triethylenetetramine (TETA) was chosen to study fluorescent variations after heating for 20 min at 175 ℃, 215 ℃ and 260 ℃, respectively. As shown in Fig. 2, maximum fluorescent wavelength position moved longer at higher temperature, this result proves that high temperature accelerates the formation of oxidized amine groups. Indeed, at 260 ℃, it took only 10 min for TETA sample to display bright fluorescence. The EEMs of TETA measured at different times in the heating process are similar to that of amine-containing polymers. Meanwhile, the fluorescent intensity of samples prepared at higher temperature is found to be relatively lower, which is probably due to the concentration quenching. Interestingly, excitation spectrum of the sample prepared at 260℃ displays two distinct bands, indicating the existence of different kinds of fluorescent centres, which agrees with the results obtained by fluorescence lifetimes.

Heat-treated TETA in water solution readily exhibited strong visible emission, which was effectively utilized to image onion cells (Fig. 3). Other polyamine analogues such as tetraethylenepentamine, putrescine and musculamine were also found to be able to emit strong fluorescence after heat treatment. Notably, it has been reported that some of them play key roles in cellular proliferation and differentiation.

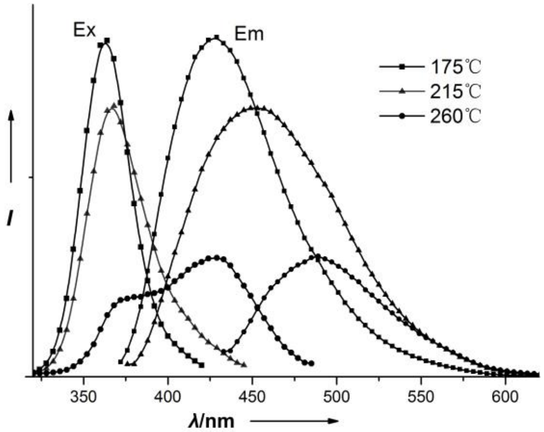

Fig. 2 Fluorescent spectra of three TETA samples prepared by heat treatment at different temperatures. All samples were measured at their maximum excitation and emission wavelength, respectively.

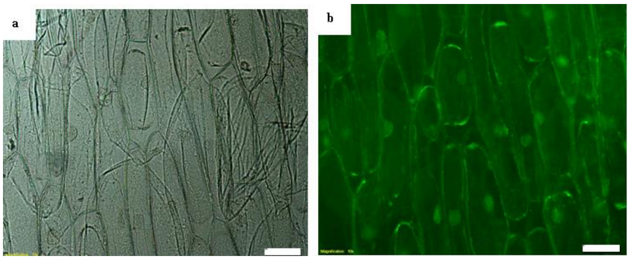

Fig. 3 Microscopic images of onion inner epidermal cells stained with heat-treated TETA. a) brightfield image, b) fluorescent image under excitation at 400 nm. Scale bars: 100 μm.

As mentioned above, a method of preparing small amine molecules with strong visible fluorescence has remained elusive, although their emission in the ultraviolet region was observed several decades ago.[10] Using 1, 2-Ethylenediamine (EDA) as an example, we confirmed that heat treatment was applicable to prepare fluorescent small amine molecules. As shown in Fig. 4, the position of fluorescence maximum wavelength of EDA was red-shifted quite remarkably in the heat process of reflux, which was akin to that of amine-containing polymer and polyamine. One interesting observation was that two peaks were detected simultaneously. The intensity of the peak at shorter wavelength decreased with the increasing of intensity of the longer one in the heating process. This result clearly demonstrates the fact that there were several fluorescent centres and they could transfer from one to another. Meanwhile, this "peak-to-peak" jump implies that the transformation from one fluorescent centre to another makes a large contribution to the red shift of fluorescent peak, relative to other possible causes such as inner-filter effect and emission-absorption overlap; otherwise, a successive change of peak position would be observed.

One of the remarkable results to emerge from this study is that the as-prepared EDA can be viewed as the "smallest" fluorescent compounds in the family of organics. Compared with current fluorescent organic compounds containing phenyl units, small amine molecules feature many attractive merits

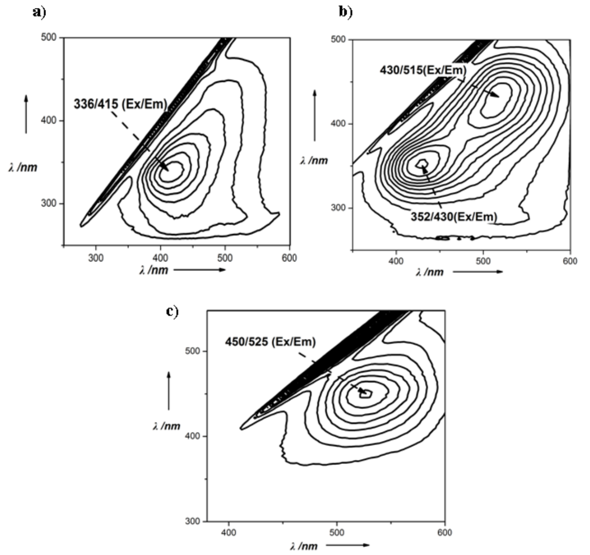

Fig. 4 Variations of fluorescent peaks of EDA in the heating process of reflux. Contour plot for the EEM of EDA measured at different times: a)11 hr, b)15 hr and c) 24 hr, respectively. Arrows indicate the position of fluorescent peaks.

such as high polarity and good permeability. Besides EDA, many kinds of small molecules containing primary, secondary or tertiary amine groups were found to fluoresce after heat treatment (Fig. S4, ESI†). In contrast to our results, previous studies concluded that primary and secondary amines could not emit fluorescence, which was interpreted by hydrogen loss via predissociation in the upper state. [8] In addition, our IR data also indicate the oxidized amines were obtained in the case of small amine molecules (Fig. S5, ESI†).

The formation of fluorescent centres in the process of heat-treatment probably undergo two steps: (a) oxidation of amine by oxidant or oxygen in air,[1b,2b,7] (b) aggregation of oxidized amine groups when their concentration become higher in heating process.[9] Particularly, the latter step (a physical change) possibly plays an important role on the red shift of fluorescent peak from the violet spectral region to the visible one with a longer heating time, and our dilution experiment of HP-PAMAM strongly supports this proposal (Fig. S2, ESI†). This phenomenon might be similar to the abnormal fluorescent observation termed as aggregation-induced emission.[11] Hence, the fluorescent mechanism of amine-containing compounds is complicated; the change from pristine materials to fluorescent ones might include both chemical and physical processes. Prasad has revealed that aggregation of PAMAM dendrimers in different solvent system controlled the intrinsic emission intensity,[2e] which might be relative to our results. Halpern has proposed the possible contribution of excimer between amine groups to the intrinsic fluorescence.[8] So far, the fluorescent centres of visible emission have not been successfully determined, although some efforts have been done in the cases of amine-containing polymers.[7,8b,12] More works are necessary before clearly elucidate this fluorescent mechanism.

In summary, the strategy of heat treatment was proved to be facile and effective way to prepare fluorescent amine-containing compounds, including small molecules, oligomers and polymers. By this way, primary, secondary and tertiary amine groups can act as all-around building blocks for design of a wide range of fluorescent compounds. Significantly, many amine-containing compounds have a close relationship to biological activity. Therefore, a novel and attractive platform of fluorescent amine-containing compounds can be established to meet the various demands of desired optical and biological properties. Finally, this facile and low-cost strategy makes it possible to fabricate fluorescent amine-containing materials on a large scale in the near future.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, IR, GPC, fluorescence lifetimes characterization, excitation emission spectra. See DOI: 10.1039/b000000x/

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