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Photoluminescence from Amino-Containing Polymer in the Presence of CO_2: Carbamato Anion Formed as a Fluorophore

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Organic photoluminescent materials are important to many applications especially for diagnosis and detection, and most of organic photoluminescent materials contain fluorophores with extended conjugated structures. Recently some of amino-containing polymers without fluorophores with extended conjugated structure are observed to be photoluminescent, and one possible cause of the photoluminescence is oxidation of the amines. Here we show that photoluminescence can be produced by exposing a typical amino-containing polymer, polyethylenimine, to carbon dioxide. We demonstrate that carbamato anion formed via the reaction between the amine and carbon dioxide is a fluorophore; and the loosely-bound protonated water molecule can increase UV absorption but reduce the photoluminescence emission. Also carbamato anion shows solvent- and excitation wavelength-dependent emission of photoluminescence. The photoluminescence profile of carbamoto anion was discussed. These results will facilitate the understanding of photoluminescence observed from amino-containing materials and the design of new fluorophores.

Photoluminescent organic compounds such as proteins[1–4] and dyes[5–8] have been explored for bioimaging[3], detection[7,8], display[9,10] and solar energy production[11,12]. Photoluminescence is a process of emission of photons occurred when fluorophores of certain compounds return from an excited state to a lower energy state, and most of the fluorophores usually have extended conjugated structures filled with delocalized electrons which absorb and emit photons, such as p-hydroxybenzylidene-imidazolidone units in fluorescent proteins, fluorescein, rhodamine, and vitamin B_2[13,14]. However, many types of amino-containing polymers, e.g., poly (amido amines)[15–25], poly(amino esters)[26,27], polyethylenimine (PEI)[28,29], polyurea dendrimer[30], without extended conjugated structures have been reported to be photoluminescent since amino-containing dendrimers were reported to be able to emit photoluminescence[19,31]. Some of these amino-containing polymers have been explored for bioimaging[15,21,25,29,32].

Regarding the photoluminescence mechanisms of these amino-containing polymers, one explanation is that oxidation of amines by oxygen in air contributes to the photoluminescence[16,20]. Considering the feasible reactions between amines and CO_2[33–36], it is natural to inquire whether the reaction between the amines and CO_2 from air contributes to photoluminescence observed from amine-containing polymers. Therefore we were motivated to investigate the photoluminescence behavior of amino-containing polymers in the presence of CO_2. Here we show that introduction of CO_2 into a solution of a typical amino-containing polymer, polyethylenimine (PEI) as described in Figure 1, can produce photoluminescence and demonstrate that carbamato anion formed via the reaction between the amine and CO_2 is the fluorophore of the photoluminescence observed. Further the photoluminescence profile of carbamato anion is investigated.

Results

PEI, one of the polymers with the highest amine content, was chosen as a typical amino-containing polymer for the investigation. A suitable UV absorption spectrum could be observed form aqueous solution of PEI containing 50 mM ethylenimine (EI) unit after CO_2 bubbling. UV-Vis absorption and photoluminescence of the solution were measured after bubbling CO_2 at a flow rate of $\sim$ 3 ml/min for 3 h followed by being kept under ambient condition for a certain time. Figure 2A(a) shows the typical UV absorption spectrum and photoluminescence

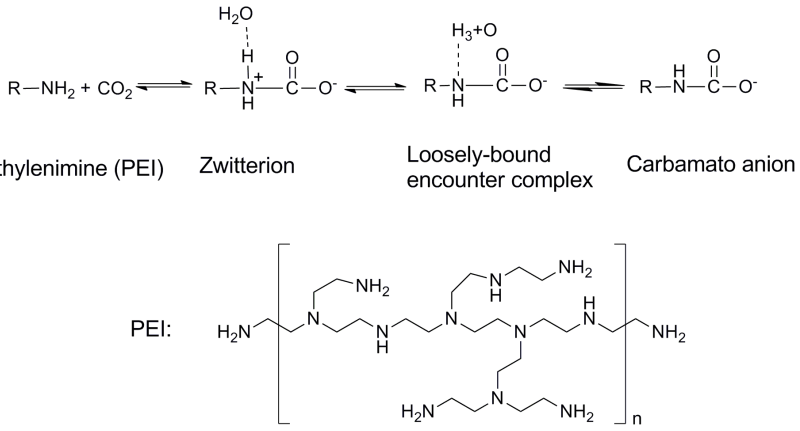

Figure 1 | **The reaction between PEI and CO_2.**

spectrum of the aqueous solution of PEI being kept for 5 days after CO_2 bubbling. Obviously a strong UV absorption at 364 nm and a strong photoluminescence emission at 470 nm with an excitation of 364 nm can be observed. In contrast, no UV absorption and relatively very weak photoluminescence with an excitation at 364 nm can be observed from the aqueous solution of PEI prepared freshly or being kept for 5 days without CO_2 bubbling as shown in Figures 2A(b) and 2A(c). Also no UV absorption and photoluminescence could be

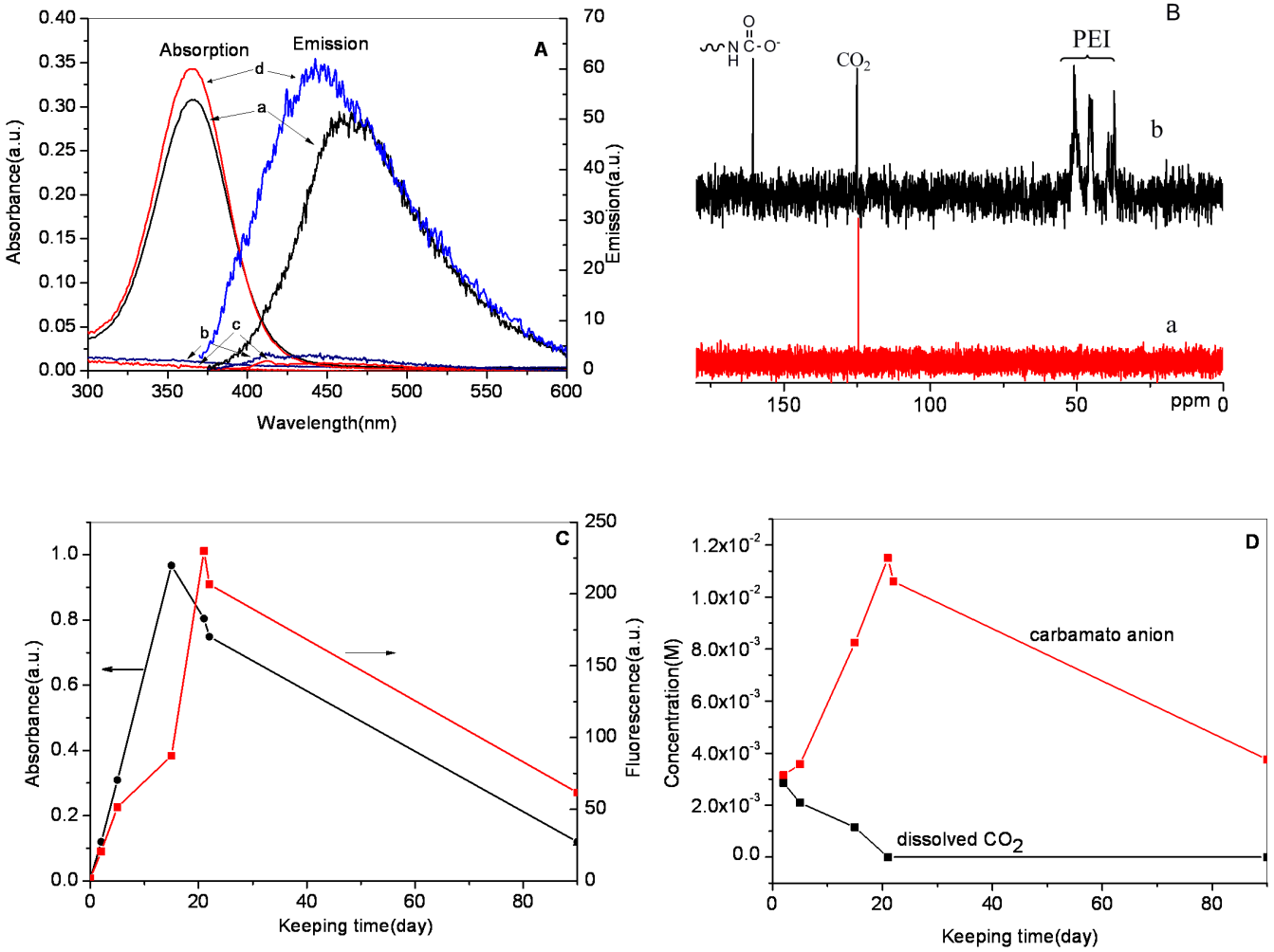

Figure 2 | (A) UV-Vis absorption and photoluminescence spectra with an excitation at 364 nm of an aqueous PEI solution containing 50 mM EI unit (a) being kept for 5 days after CO_2 bubbling in H_2O; (b) prepared freshly in H_2O; (c) being kept for 5 days without CO_2 bubbling in H_2O; and (d) being kept for 5 days after CO_2 bubbling in D_2O. (B) ^{13}C NMR spectra of (a) D_2O after CO_2 bubbling and (b)a solution of PEI in D_2O containing 50 mM EI unit being kept for 5 days after CO_2 bubbling. (C) Effect of keeping time on the UV-Vis absorption intensity and photoluminescence intensity with an excitation at 364 nm of aqueous PEI solution containing 50 mM EI unit after CO_2 bubbling. (D) Effect of keeping time on the concentration of carbamato anion and dissolved CO_2 in a solution of PEI in D_2O containing 50 mM EI unit after CO_2 bubbling.

observed from water solution bubbled with CO_2, and an aqueous solution of PEI containing 50 mM EI unit after bubbling with N_2 to removing O_2 or at pH 7.0 close to pH value after CO_2 bubbling. Therefore the strong UV absorption and photoluminescence are caused by introducing CO_2 into the aqueous solution of PEI.

As described in Figure 1, the reaction between amine and CO_2 forms cabamato anion via intermediates possibly composed of the loosely-bound encounter complex and zwitterions[37–39]. Here ^{13}C NMR was applied to monitor the formation of carbamate in a solution of PEI in D_2O bubbled with CO_2. Figure 2B(b) is ^{13}C NMR spectrum of a solution of PEI in D_2O containing 50 mM EI unit being kept for 5 days after CO_2 bubbling. The peak at 125 ppm is attributed to the dissolved CO_2, the only peak observed in ^{13}C NMR spectrum of D_2O bubbled with CO_2 as shown in Figure 2B(a). The peak attributed to the carbamato anion appears at 160 ppm[7,33,40], and the molar ratio of carbamato anion to the EI unit is determined to be ca. 7.1 : 100 (see supplementary information). In a contrast experiment, $Ba(OH)_2$ was added to check whether HCO_3^{-1} was formed based on that $BaCO_3$ is insoluble and barium carbamate is soluble[36]. The addition of $Ba(OH)_2$ showed almost no effect on ^{13}C NMR spectrum, so the amount of HCO_3^{-1} formed is negligible. This is reasonable because the kinetic reaction constant of carbamate formation is five orders of magnitude higher than that of HCO_3^{-1} formation[34,37,38]. There are three types of amine in PEI, i.e., primary amine, secondary amine and tertiary amine with a molar ratio of ca. 1 : 2 : 1 determined from ^{13}C NMR spectrum (see supplementary information). On the basis of the previous work, the reactivity sequence of three types of amine should be primary amine > secondary amine > tertiary amine[41]. Therefore the carbamate was formed via the reaction between the primary amines of PEI and CO_2 as described in Figure 1. Bubbling CO_2 into water produced no UV absorption and photoluminescence, hence the carbamate formed is the fluorophore of the photoluminescence observed.

As shown in Figure 2C, both UV absorption peak intensity and photoluminescence intensity from the aqueous solution of PEI bubbled with CO_2 change with the keeping time after CO_2 bubbling. The peak intensity of UV absorption at 364 nm increases with the keeping time before reaching the maximum after being kept for 15 days and then decrease during the observation up to 90 days. Similarly the photoluminescence intensity at 470 nm increases before reaching the maximum after being kept for 21 days and then decreases. Meanwhile Figure 2D shows the effect of the keeping time on the concentration of the carbamato anion and the dissolved CO_2 which were determined from ^{13}C NMR spectra (see supplementary information). The concentration of carbamato anion reaches the maximum after being kept for 21 days and then decreases. When the concentration of carbamato anion reaches the maximum, the molar ratio of carbamato anion to the EI unit is 23 : 100, so the carbamato anion is still formed via the reaction between the primary amine of PEI and the dissolved CO_2. Meanwhile the concentration of dissolved CO_2 decreases continuously after CO_2 bubbling until being undetectable at 21 days. The consistent reducing concentration of the dissolved CO_2 should be due to the reaction with amine and evaporation into the environment. When the dissolved CO_2 concentration decreases to a certain level, the amount of carbamate starts to decrease due to decarboxylation. Figures 2C and 2D show that there is a coherent relationship between the photoluminescence intensity and the concentration of carbamato anion which further confirms that carbamato anion is the fluorophore of the photoluminescence observed.

Also Figure 2C reflects that there is a discrepancy between the effect of keeping time on the UV absorption intensity and the photoluminescence intensity. While the maximum of UV absorption is obtained after being kept for 15 days, the photoluminescence intensity reaches the highest value at 21 days. These indicate that there are more than one type of fluorophore contributing to UV absorbance

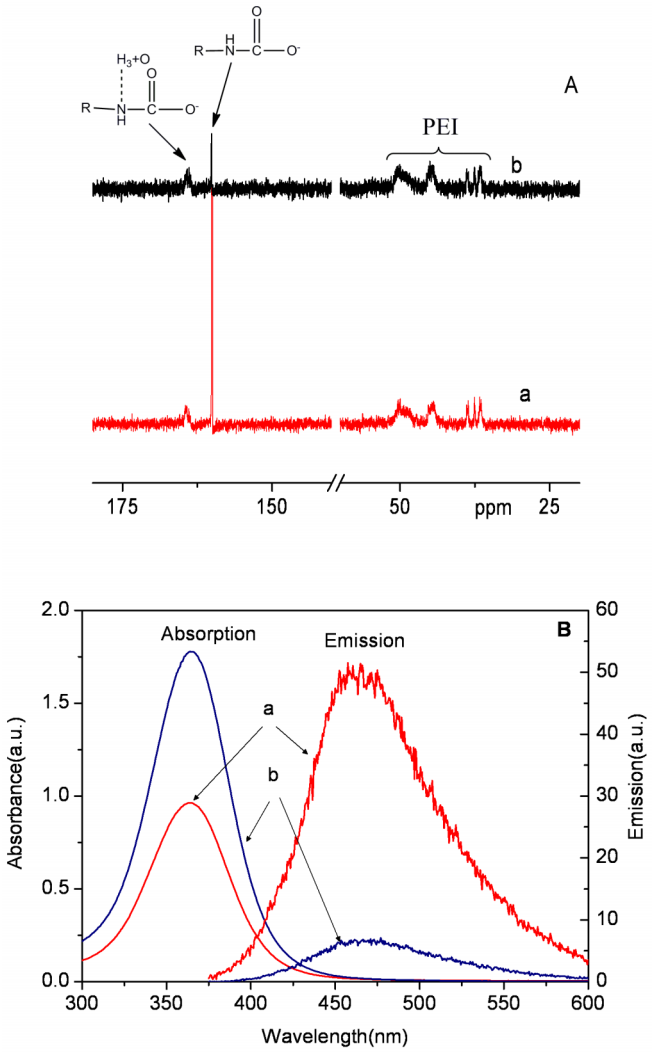

Figure 3 | (A) ^{13}C NMR spectra of a solution of PEI in D_2O containing 4.6 M EI unit being kept for 15 days after CO_2 bubbling (a) before and (b) after thermal treatment at 60°C for 3 h under N_2. (B) UV-Vis absorption and photoluminescence spectra with excitation at 364 nm of an aqueous solution of PEI containing 50 mM EI unit being kept for 15 days after CO_2 bubbling (a) before and (b) after thermal treatment at 60°C for 3 h under N_2.

and photoluminescence; otherwise a unanimous variation tendency should be observed. The other types of fluorophore should be the intermediates of carbamato anion formed when the dissolved CO_2 was still presented. However no corresponding peaks can be observed in Figure 2B(b) even though the ^{13}C NMR spectrum was collected for 3 days due to a high ratio of noise to signal caused by the low concentration of PEI. In order to reduce the ratio of noise to signal, the concentration of PEI was increased by around 100 times to containing 4.6 M EI unit. Figure 3A(a) shows the ^{13}C NMR spectrum of the solution of PEI in D_2O containing 4.6 M EI unit being kept for 15 days after CO_2 bubbling (also formation of HCO_3^- under this condition is negligible indicated by the insignificant effect of adding $Ba(OH)_2$ on the ^{13}C NMR spectrum.). In comparison with Figure 2B(b), a new broad peak appears at 164 ppm. This peak is ascribed to the loosely-bound encounter complex rather than zwitterions because the down-field shifting of the peaks attributed to carbon in the zwitterions should be more due to the positively charged nitrogen. The loosely-bound encounter complex with a different bound degree results in the broad peak in the ^{13}C NMR

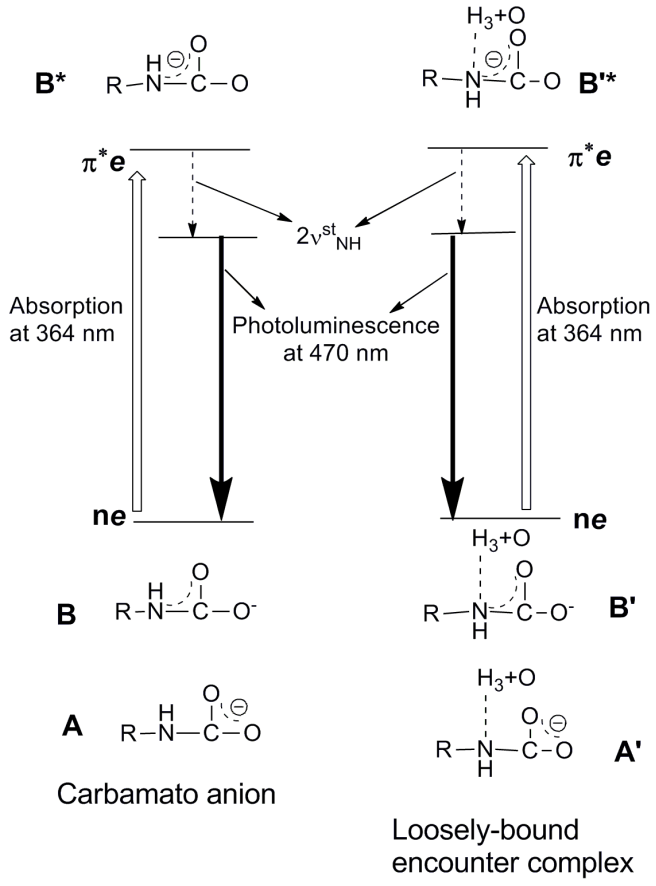

Figure 4 | **Photoluminescence profile of carbamato anion.**

spectrum. Therefore, the loosely-bound encounter complex is the dominant intermediate of carbamato anion as reported[39]. Hence both carbamato anion and the loosely-bound encounter complex contribute to the photoluminescence observed.

We found that thermal treatment could change the equilibrium between carbamato anion and the loosely-bound encounter complex; therefore thermal treatment was applied to differentiate the photoluminescent behaviors of carbamato anion and the loosely-bound encounter complex. Figure 3A shows ^{13}C NMR spectrum of the solution of PEI in D_2O containing 4.6 M EI unit being kept for 15 days after CO_2 bubbling before and after thermal treatment at 60°C for 3 h under N_2. The molar ratio of the loosely-bound encounter complex to carbamato anion is shown to increase from 1.76 to 1.94 with the molar ratio of the total carbamate to the EI unit being kept at ca. 35 : 100 (see supplementary information). So the thermal treatment shifts the equilibrium towards the formation of the loosely-bound encounter complex (the degradation of carbamate to recover amines and remove CO_2 occurs at 100°C above[33]). Accordingly, the effects of thermal treatment at 60°C for 3 h under N_2 on the UV absorption and photoluminescence of aqueous solution of PEI containing 50 mM EI unit being kept for 15 days after CO_2 bubbling was investigated. As shown in Figure 3B, the thermal treatment reduces photoluminescence intensity at 470 nm from 1.75 a.u. to 0.17 a.u. but increases the UV absorption at 364 nm from 0.8 a.u. to 1.8 a.u. Hence the loosely binding of H_3^+O to carbamato anion results in a higher UV absorption but a lower photoluminescence emission.

Discussion

As shown in Figure 4, there are two 3- atoms (either N, C and O or 2 O and C) containing resonance structures, i.e., A and B, for carbamato anion, without instable π-conjugated 4-atoms containing (N, C and 2 O) resonance structures with one anti-bonding orbital being filled with electrons[42–47]. Accordingly, there are two resonance structures for the loosely-bound encounter complex, i.e., A′ and B′. Among these resonance structures, A and A′ are the major components because O atom is more electronegative than N atom. However, n → π* transition should only occur in B and B′ with n electron from the negatively charged O atom jumping to the conjugated unit composed of N, C and O atoms, but is prohibited in A and A′ due to electronic repulsion between n electron of N atom and electrons on the carboxylate ion. Hence B and B′ are the dominant fluorophores. The n → π* transition of B and B′ under UV irradiation is supported by the red-shift in UV absorption from 364 nm

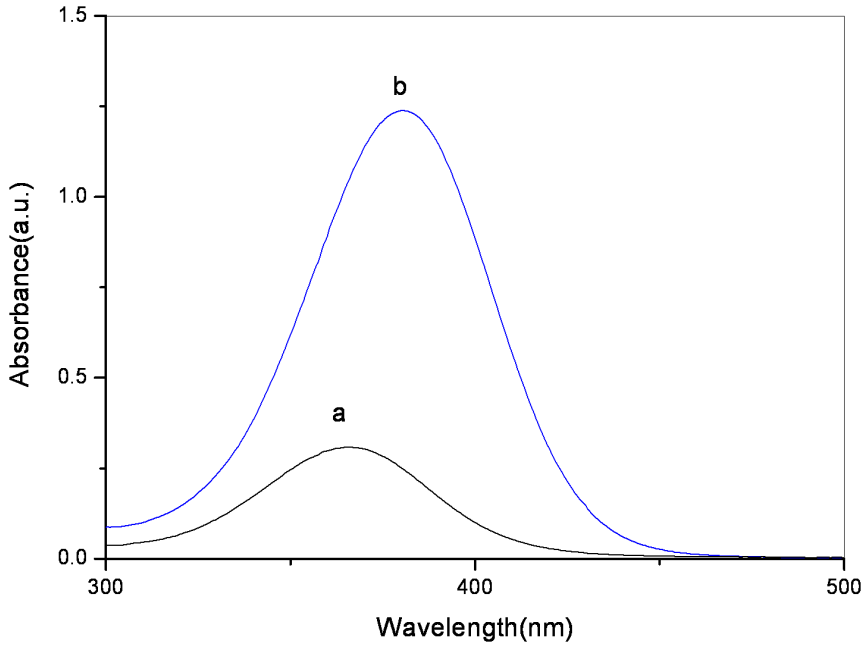

Figure 5 | **UV-Vis absorption of a solution of PEI containing 50 mM EI unit being kept for 5 days after CO_2 bubbling in (a) water and (b) methanol.**

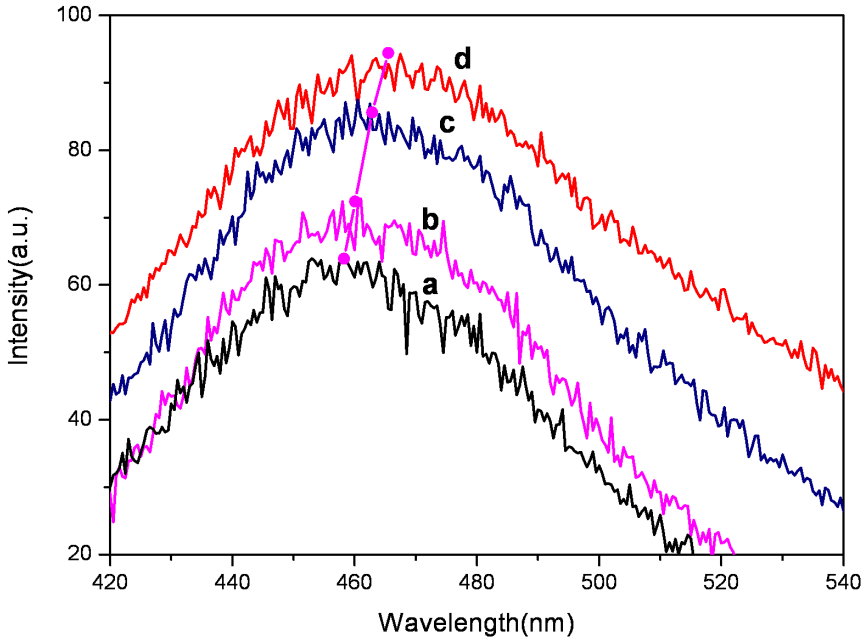

Figure 6 | Photoluminescence emission spectra of an aqueous solution of PEI containing 50 mM EI unit being kept for 10 days after CO_2 bubbling being excited at (a) 330 nm; (b) 340 nm; (c) 350 nm; and (d) 360 nm.

to 380 nm when water is substituted by methanol as shown in Figure 5, because n → π* transition shows a red-shift and π→π* transition shows a blue-shift reversely when solvent molecules have lower polarity and form hydrogen bonding with a lower strength[14], and methanol has a lower polarity and forms a weaker hydrogen bonding with carbamate than water[48,49]. In comparison with B, the loosely-bound H_3^+O in B′ facilitates the n → π* transition of electron, and the H_3^+O in the excited state B′* reduces the feasibility of relaxation of the exited electrons. These should be the cause of the stronger UV absorption but a weaker photoluminescence emission observed for carbamato anion loosely bonded with H_3^+O.

As shown in Figure 2A, the frequency difference between the excitation at 364 nm (wavenumber: 27472 cm^{-1}) and the emission at 470 nm (wavenumber: 21276 cm^{-1}) is 6196 cm^{-1}. This difference is ca. two times of the stretching vibration frequency of N-H (ν^{st}_{NH}) or O-H (ν^{st}_{OH}) which are ca. 3300 cm^{-1} as reflected in FTIR spectrum of aqueous solution of PEI (see supplementary information Fig. S4). When H_2O is substituted by D_2O, Figure 2A(d) shows that the emission peaks shift to 442 nm (wavenumber: 22624 cm^{-1}), with the emission peak being kept at 364 nm. The frequency difference between excitation at 364 nm (wavenumber: 27472 cm^{-1}) and the emission peaks are 4848 cm^{-1} which are close to two time of the vibration frequency of N-D (ν^{st}_{ND}) or O-D (ν^{st}_{OD}) of ca. 2400 cm^{-1} as shown in FTIR (see supplementary information Fig. S4). Further, Figure 6 shows a typical excitation wavelength-depend photoluminescence profile, which was obtained from an aqueous solution of PEI containing 50 mM EI unit being kept for 10 days after CO_2 bubbling. The photoluminescence emission wavelength depends on the excitation wavelength with the frequency difference between the excitation and the emission being almost kept constant to be two times of ν^{st}_{NH} or ν^{st}_{OH}. So one important nonradiative process of the excited B* and B′* is via stretching vibration of N-H or O-H[50], and preferably via the intramolecular N-H of carbamato anion in comparison with the O-H of water[13,14].

In order to understand the functions of polymer morphology in the photoluminescence observed, butylamine was adopt to substitute PEI, and the solution of butylamine in methanol was prepared. No UV absorption could be observed from a solution of 50 mM butylamine in methanol being kept for 5 days after CO_2 bubbling (see supplementary information Fig. S5). However, carbamate was formed as reflected in ^{13}C NMR spectrum of a solution of 4.6 M butylamine in methanol being kept for 5 days after CO_2 bubbling (see supplementary information Fig. S6). So fluoresecence quenching of small carbamate easily occurs, and polymer morphology is important in avoiding the fluorescence quenching of all the conjugated carbamate.

Photoluminescence can be produced by exposing aqueous solution of PEI to CO_2. Carbamato anion formed via the reaction between the amines of PEI and CO_2 contribute to the photoluminescence. The loosely binding of H_3^+O to carbamto anion results in a higher UV absorption and a lower photoluminescence emission, probably due to a facilitated n → π* transition and a retarded relaxation of the excited electron. The photoluminescence emission wavelength of carbamato anion depends on the solvent type and the excitation wavelength, and the nonradiative process is via stretching vibration of the N-H in the carbamato anion. Considering the common existence of CO_2, the reaction with CO_2 should be one of the causes of photoluminescence observed from amino-containing polymers.

Methods

Materials. Hyperbranched Poly(ethyleneimine) (PEI) (M_n: 600), butylamine, barium hydroxide, methanol, and deuterium oxide (D_2O) were purchased from Aldrich and used as received.

Characterization techniques. ^{13}C NMR spectra were recorded on a Bruker ACF 400 FT-NMR spectrometer. The absorption and photoluminescence spectrum measurements were conducted on a Shimadzu UV-1601 PC UV-Vis spectrophotometer and a Perkin-Elmer Instrument LS 55 luminescence spectrometer, respectively. In order to get comparable photoluminescence intensity, all experimental parameters were kept fixed for all emission scans. FT-IR spectra of PEI solution on CaF_2 plate were collected in a frequency range of 1000–4000 cm^{-1} with 2 cm^{-1} resolution and 64 scans on a FTIR spectrometer Spectrum 2000 (Perkin Elmer) in a transmission mode.

Exposed PEI to CO_2. For UV-Vis absorbance and photoluminescence scans, CO_2 was introduced to a solution of PEI containing 50 mM EI in 10 ml of water or methanol in a 20 ml vial at a flow rate of ~ 3 ml/min for 3 h using a one needle-inlet and one needle-outlet configuration. Then the solution was kept for a designed time before measurements. For ^{13}C NMR experiments, D_2O was used instead and the concentration of EI unit was 50 mM and 4.6 M, respectively.

Thermal treatment procedure. Aqueous solution of PEI containing 50 mM EI being kept for 15 days after CO_2 bubbling was put into an oil bath at 60°C under nitrogen for 3 hours before UV-Vis absorbance and photoluminescence scan were conducted. For ^{13}C NMR experiment, a solution of PEI in D_2O containing 4.6 M EI unit was heated at 60°C for 3 hours under nitrogen just before NMR experiment. All UV-Vis absorbance measurement, photoluminescence scan and NMR experiments were finished in less than 5 minutes.

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Author contributions

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Additional information

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