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Clustering-triggered Emission of Cellulose and Its Derivatives

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Electronic Supplementary Information

Abstract In recent years, nonconventional luminogens free of aromatic groups have attracted extensive attention due to their academic importance and promising wide applications. Whilst previous studies generally focused on fluorescence from aliphatic amine or carbonyl-containing systems, less attention has been paid to room temperature phosphorescence (RTP) and the systems with predominant oxygen functionalities. In this work, photophysical properties of the polyhydroxy polymers, including microcrystalline cellulose (MCC), 2-hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), and cellulose acetate (CA), were studied and compared. While MCC, HEC, and HPC solids showed bright emission alongside distinct RTP, CA demonstrated relatively low intensity of solid emission without noticeable RTP. Their emissions were explained in terms of the clustering-triggered emission (CTE) mechanism and conformation rigidification. Additionally, on account of its intrinsic emission, concentrated HEC aqueous solution could be used as the probe for the detection of 2,4,6-trinitrophenol (TNP).

Keywords Cellulose; Nonconventional luminogens; Room temperature phosphorescent; Clustering-triggered emission

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INTRODUCTION

Luminescent polymers are promising for applications in organic light emitting diodes, biosensing, bioimaging, diagnosis, and therapy.^[1–4] Conventional luminescent polymers contain fluorophores with remarkable conjugates, *i.e.* (hetero)aromatics and alternating single and multiple bonds. Recently, some nonconventional emissive polymers without traditional fluorophores are attracting increasing attention.^[5–12] They normally contain electron rich moieties and can be natural products, synthetic compounds, and biomolecules, which generally own concentration-enhanced emission and aggregation-induced emission (AIE) characteristics.^[13–17] In comparison to their conventional counterparts, they own such merits as facile preparation, good processability, film-forming ability, and moreover, outstanding biocompatibility, which render them highly potential for sensing, lightning, encryption, and biological applications. Their emission mechanism, however, is still under debate. Many hypotheses have been proposed for diverse systems.

While they might be sound for their specific cases, they are inapplicable to other systems. Recently, we proposed the clustering-triggered emission (CTE) mechanism to rationalize the unique photophysical behaviors of nonconventional luminophores.^[5] In other words, the clustering of nonconventional chromophores which bear π and lonepaired (n) electrons and subsequent overlapping of electron cloud together with simultaneous conformation rigidification are responsible for the intrinsic light emission. CTE mechanism can not only explain our own systems but also well interpret other systems. Meanwhile, both small molecules and polymers, including nonaromatic amino acid,^[18] cyanoacetic acid,^[19] poly(ether amine)s,^[20] poly(amino ester)s,^[21] poly(amino acid)s,^[18] polyureas,^[22] and polyacrylonitrile,^[23] were reported to display CTE characteristics. So far, most investigations concern on the fluorescence of nonconventional luminogens,^[24–29] whereas little attention has been paid to their room temperature phosphorescence (RTP). Such a situation might be caused by the difficulty to achieve pure organic RTP due to the spin-forbidden nature of single-triplet transitions, thermal deactivation, and chemical quenching during the long lifetime of triplets.^[30]

In 2010, Tang and coworkers reported a new phenomenon of crystallization-induced phosphorescence (CIP) of pure organic luminogens at room temperature.^[31] The CIP phenomenon is ascribed to the highly rigidified conformations

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in crystals owing to the presence of effective intermolecular interactions, which significantly frustrate the intramolecular motions. Meanwhile, crystal lattices also isolate triplet excitons from environmental quenchers (*i.e.* oxygen and moisture), thus lighting up the RTP emission. Therefore, the essence of CIP phenomenon is conformation rigidification together with isolation from quenchers.

We are interested in the exploration of emission mechanism of nonconventional luminogens and novel RTP emitters. Previously, we reported intriguing emission and moreover RTP from crystalline rice, cellulose, starch, *etc.*^[32] Herein, to gain more insights into the emission mechanism and the origin of RTP, we thoroughly studied the photophysical properties of microcrystalline cellulose (MCC) and its derivatives, namely 2-hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), and cellulose acetate (CA) (Chart 1). Except CA, all other three polymers exhibited remarkable emissions including RTP. The phosphorescence emission peaks and lifetimes ($\langle\tau\rangle$) of MCC/HEC/HPC were 500/500/497 nm and 20.41/0.66/0.27 ms, respectively. Additionally, as an example, HEC was used for the detection of 2,4,6-trinitrophenol (TNP).

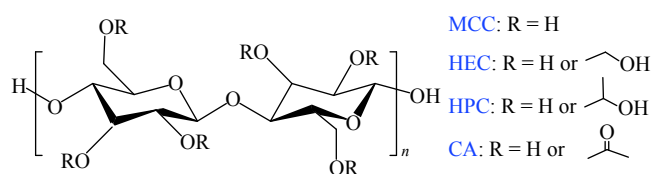


Chart 1 Chemical structures of MCC, HEC, HPC, and CA

EXPERIMENTAL

Materials

MCC, HEC, HPC, and CA were purchased from Sigma-Aldrich. TNP was obtained from Adamas Reagent Co., Ltd. Distilled water was prepared by Milli-Q Pure Water instrument. MCC was further purified with 5 wt% NaOH solution for 24 h to remove lignin, and then washed with deionized water to neutral. The other cellulose derivatives were purified using the dissolution-precipitation method; water/THF (for HEC, HPC) and acetone/water (for CA) were used as the solvent/nonsolvent. All samples were dried in vacuum at 50 °C for 24 h before tests. Other commercially available reagents were used without further purification.

Characterization

Fluorescent and phosphorescent spectra were taken on Horiba FluoroMax-4 and Varian Cary Eclipse fluorescence spectrophotometers, respectively. Absorption spectra were recorded on a Shimadzu UV-3600 Plus UV-VIS-NIR spectrophotometer. Powder X-ray diffraction (XRD) analyses were performed on an X'Pert PRO X-ray diffractometer. Polarized optical images were captured under an Eclipse E200 POL microscope.

Preparation of Fluorescence Assay for TNP Detection

Aqueous HEC (5.0 mg·mL⁻¹) and TNP (1.0 × 10⁻² mol·L⁻¹) solutions were prepared with distilled water. Then 10 μL of TNP aqueous solution (1 × 10⁻² mol·L⁻¹) was added to 2 mL of HEC aqueous solution every time, and the emission spectra of different mixtures were determined.

RESULTS AND DISCUSSION

Photophysical Properties of MCC, HEC, HPC, and CA powders

Cellulose, a natural polymer with the formula of (C₆H₁₀O₅)_n, is a polysaccharide consisting of a linear chain with several hundreds to many thousands of β (1→4) linked D-glucose units. It owns extensive sources, excellent biocompatibility, and good processability. Therefore, cellulose-based luminescent materials may have more advantages in bio-related applications. Fig. 1 shows the luminescent photographs of MCC, HEC, HPC, and CA powders under 365 nm UV light. While MCC, HEC, and HPC emitted blue lights at ambient conditions, CA did not. To gain deeper insights into the nature of the emission, photoluminescence (PL) spectra of the solid samples were collected. As shown in Fig. 2(a), UV-Vis absorption and fluorescence emission peaks of MCC powders are located at 285 and 415 nm, respectively. The PL quantum efficiency of MCC was determined to be 4.4%. It is also noted that MCC powders demonstrated varying emission profiles with different excitation wavelengths (λ_{ex}) (Fig. S1, in electronic supplementary information, ESI), thus highly indicative of the existence of diverse emission species. Delayed PL spectrum of MCC powders was obtained through time-gated technology with a delay time (t_d) of 1.0 ms after the stop of excitation, which peaks at around 500 nm (Fig. 2b). The large difference of 85 nm between the maxima of prompt and delayed emissions highly indicates that the delayed emission was RTP rather than delayed fluorescence (DF). To further confirm it, time-resolved decay curve at 500 nm was recorded, which shows the $\langle\tau\rangle$ value of 20.41 ms (Fig. 2c), thus duly suggesting its RTP nature.

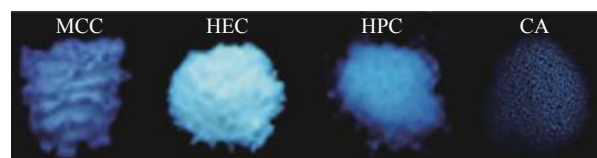


Fig. 1 Photographs of MCC, HEC, HPC, and CA powders taken under 365 nm UV irradiation

The phosphorescence spectra of MCC powders at 77 K were also measured for comparison. As shown in Fig. 2(d), it is interesting that the phosphorescent emission wavelength gradually red-shifted with an increase in λ_{ex} , exhibiting obvious a λ_{ex} -dependent phosphorescence. When excited at 280 nm, it displayed an emission maximum at 467 nm. With increasing λ_{ex} , the emission maximum gradually red-shifted, accompanying with the decreased intensity. Notably, the emission color also varied from sky blue (467 nm) to spring green emission (520 nm) with 280 and 360 nm UV radiation (Fig. S2, in ESI). This phenomenon is consistent with the observations in previously reported nonconventional luminogens of sodium alginate, poly(acrylic acid) (PAA), polyacrylamide (PAM), and poly(*N*-isopropylacrylamide),^[6,33] which highly indicated the presence of diverse emissive species.

The green phosphorescence emission of MCC powders prompted us to explore the photophysical properties of other

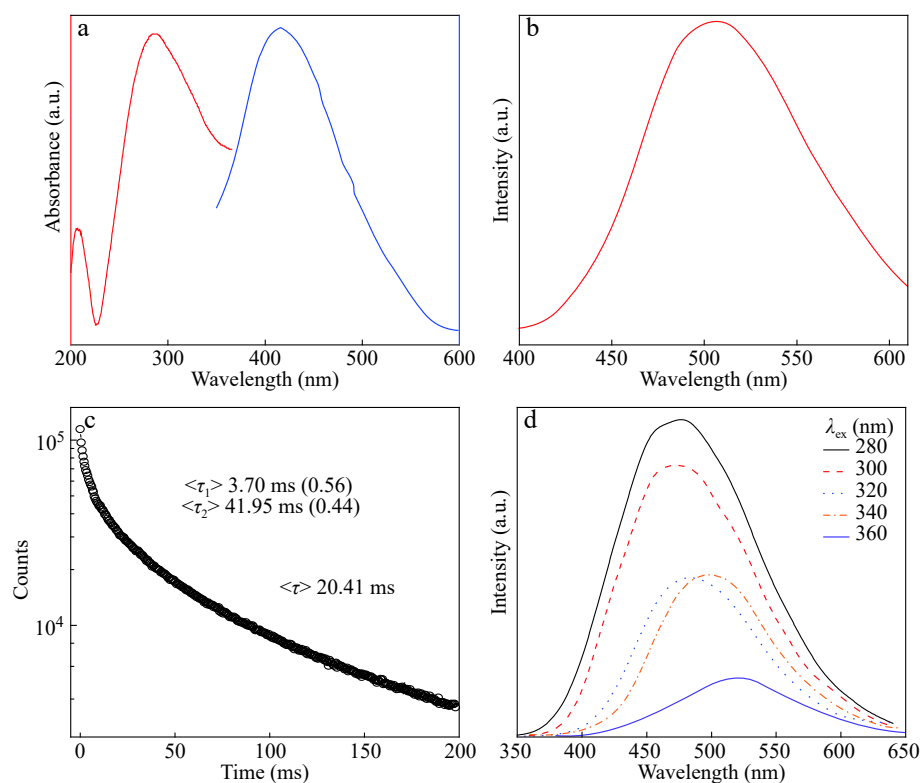


Fig. 2 (a) UV-Vis absorption and emission spectra of MCC powders ($\lambda_{\text{ex}} = 330$ nm); (b) RTP spectrum ($\lambda_{\text{ex}} = 330$ nm) and (c) lifetime (@ 500 nm) of MCC powders; (d) Delayed emission spectra of MCC solids at 77 K with different λ_{ex} s

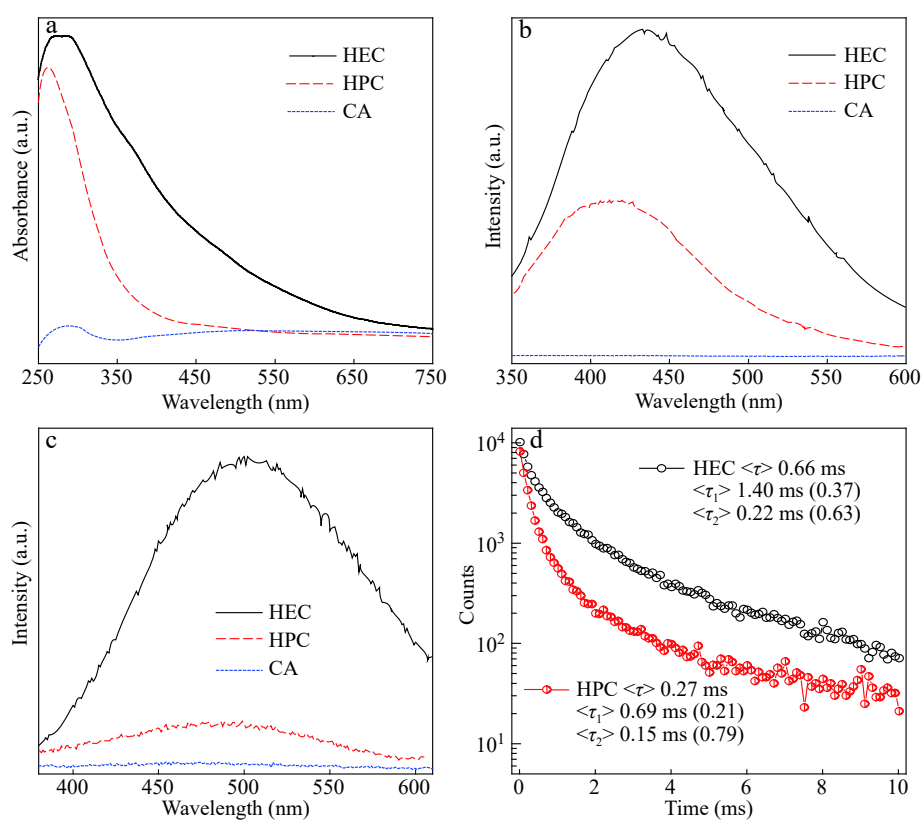


Fig. 3 (a) UV-Vis absorption, (b) prompt emission ($\lambda_{\text{ex}} = 330$ nm), and (c) delayed emission ($t_d = 1.0$ ms, $\lambda_{\text{ex}} = 330$ nm) spectra of HEC, HPC, and CA powders at room temperature; (d) Lifetime of HEC and HPC powders at room temperature

cellulose derivatives. Similar phenomena were also observed for HEC and HPC powders, whose maxima of absorption, prompt emission, and delayed emission ($t_d = 1.0$ ms) were 278, 433, 500 nm and 262, 413, 497 nm, respectively (Figs. 3a–3c). To quantitatively evaluate the emissions, solid efficiencies of the luminogens were determined, which were 3.2% and 3.8% for HEC and HPC, respectively. Time-resolved emission decay experiment revealed the $\langle\tau\rangle$ values of 0.66 and 0.27 ms for the delayed emissions of HEC and HPC solids (Fig. 3d), respectively, which could verify their phosphorescent nature. However, CA powders only exhibited a weak absorption peak at ~ 285 nm, and no remarkable fluorescence or phosphorescence peak could be observed, which is consistent with the faint emission shown in Fig. 1. In other words, MCC, HEC, and HPC powders owned RTP emissions, while CA powders did not. However, at 77 K, intense emission along with persistent phosphorescence was clearly noticed for the CA powders (Figs. S3 and S4, in ESI). These results imply that the faint emission of CA at room temperature might be ascribed to the effective molecular motions.

Photophysical Properties of HEC and HPC Solutions

Owing to the insolubility of MCC in common solvents, herein, we only investigated the photophysical properties of HEC and HPC solutions. As shown in Fig. 4(a), the emission of HEC solution was progressively enhanced as the concentration increased, displaying a concentration-enhanced emission feature, which can also be seen from the vivid image contrast in Fig. 4(c). The emission maximum at ~ 450 nm, however, varied little with concentration. HPC aqueous solutions showed similar concentration enhanced emission feature, with the emission peak at 450 nm (Fig. 4b, Figs. S5 and S6, in ESI). However, unlike HEC and HPC, the emission of different CA solutions was rather weak, whose emission signals are even parallel to the baseline (Fig. S7, in ESI). To gain more insights, absorptions of HEC and HPC aqueous solutions were recorded, whose intensities also increased with a tail extended to much longer wavelengths, along with the increase of concentration (Figs. S8 and S9, in ESI).

Emission Mechanism Understanding

Preceding results clearly suggest the intrinsically emissive nature of MCC, HEC, and HPC in solids and concentrated solutions at room temperature, despite the lack of conventional chromophores with large conjugations. By contrast, CA shows relatively weak emission in the solid states. Considering the neglectable emissions of their dilute solutions, and enhanced emission in concentrated solutions and solids, their emission can be rationalized by the CTE mechanism. The clustering of ether, hydroxyl, and carbonyl moieties provide effective through space intra- and intermolecular interactions among them. Therefore, extended electron delocalization is formed, which can be excited to generate radiative emission with rigidified conformations. As can be seen from Chart 1, HEC, HPC, and CA are MCC derivatives with hydroxyls being partially replaced by hydroxyethyl, hydroxypropyl, and acetyl groups, respectively. As a result, all side chains of MCC, HEC, and HPC

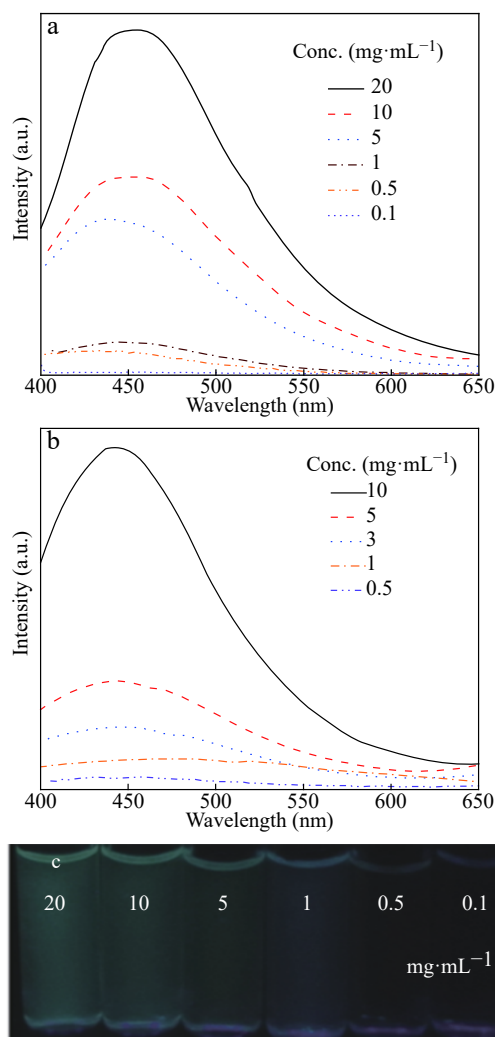


Fig. 4 PL spectra of the aqueous solutions of (a) HEC and (b) HPC at different concentrations ($\lambda_{\text{ex}} = 310$ nm); (c) Photographs of varying HEC solutions taken under 365 nm UV light

contain a large number of hydroxyl units, while CA side chain possesses fewer hydroxyls, which might be predominantly responsible for its relatively weak emission in the solid state. That is because, hydrogen bonds, on the one hand, can rigidify molecular conformations, on the other hand, can facilitate the short contact of nonconventional chromophores, thus beneficial to the light emission. It is also supported by the boosted emission and the emergence of persistent phosphorescence of CA solids at 77 K.

Further XRD measurement shows obvious diffraction peaks at $15.50^\circ/22.40^\circ/34.40^\circ$, 20.90° , and $8.50^\circ/20.1^\circ$ for the solid powders of MCC, HEC, and HPC, respectively, whereas there are several weak and broad diffractions for CA powdered (Fig. 5a). These results indicate CA owned the lowest crystallinity, which is also verified by the observation on the polarized optical microscopy (POM) images (Fig. 5b). Hence, the weak solid emission of CA probably stemmed from its fewer hydrogen bonds and poor crystallinity, which are unfavorable for the light emission.

Furthermore, n electrons of oxygen atoms could promote the $n-\pi^*$ transition, spin-orbital coupling, and consequently

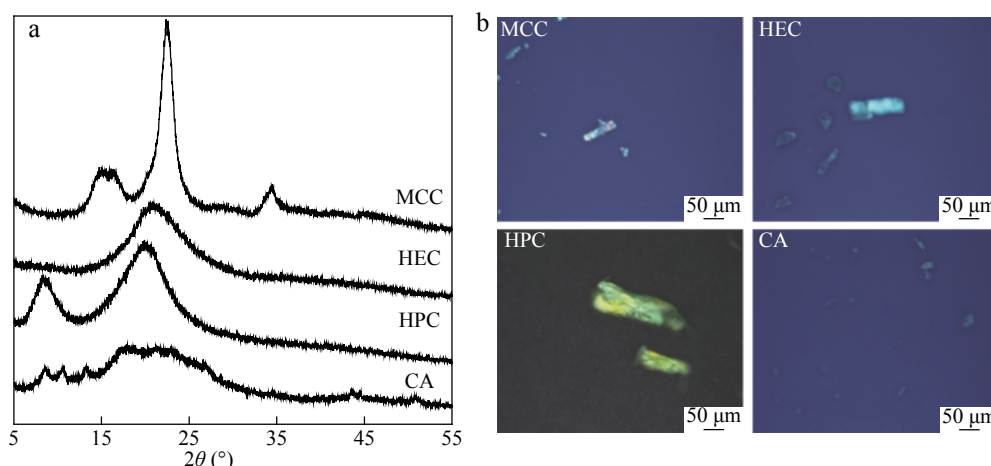


Fig. 5 (a) XRD patterns and (b) POM images for the solid powders of MCC, HEC, HPC, and CA

intersystem crossing (ISC) process, thus favorable for the generation of RTP emission.^[5] It is also noted that clustering of the nonconventional chromophores enriches energy levels of both excited single and triplet states, which may narrow their energy gaps, thus promoting the ISC processes. Combining all the above discussions, the emission processes of MCC and its derivatives can be illustrated as Fig. 6, wherein clustering of diverse subunits ($-O-$, OH , or $C=O$), extended delocalization with enrich energy levels, and conformation rigidification are emphasized.

Detection of TNP by HEC

TNP, a well-known nitroaromatic explosive, can contaminate groundwater and soil, while damaging skin, eyes, and respiratory systems of human beings and wildlife.^[34–36] Therefore, sensitive detection of TNP is of crucial impor-

tance in view of public security, environmental protection, and human health. To test whether the above polymers can be used for the detection of TNP, HEC was selected as a representative. As can be seen from Fig. 7(a), with incremental addition of TNP, the PL intensity of HEC aqueous solution ($5 \text{ mg} \cdot \text{mL}^{-1}$) continuously decreases, and is almost quenched with the TNP concentration of $0.57 \text{ mmol} \cdot \text{L}^{-1}$. From the Stern-Volmer plot (Fig. 7b), it is clear that the TNP quenching effect can be divided into two phases. When TNP concentration is not higher than $0.24 \text{ mmol} \cdot \text{L}^{-1}$, the plot is linear with a $K_{\text{SV,I}}$ value of 43.5. When the TNP concentration is above $0.24 \text{ mmol} \cdot \text{L}^{-1}$, however, the other linear plot with a $K_{\text{SV,II}}$ value of 325.6 is observed, exhibiting an amplified quenching effect. Therefore, HEC was a potential environment-friendly probe for the detection of TNP.

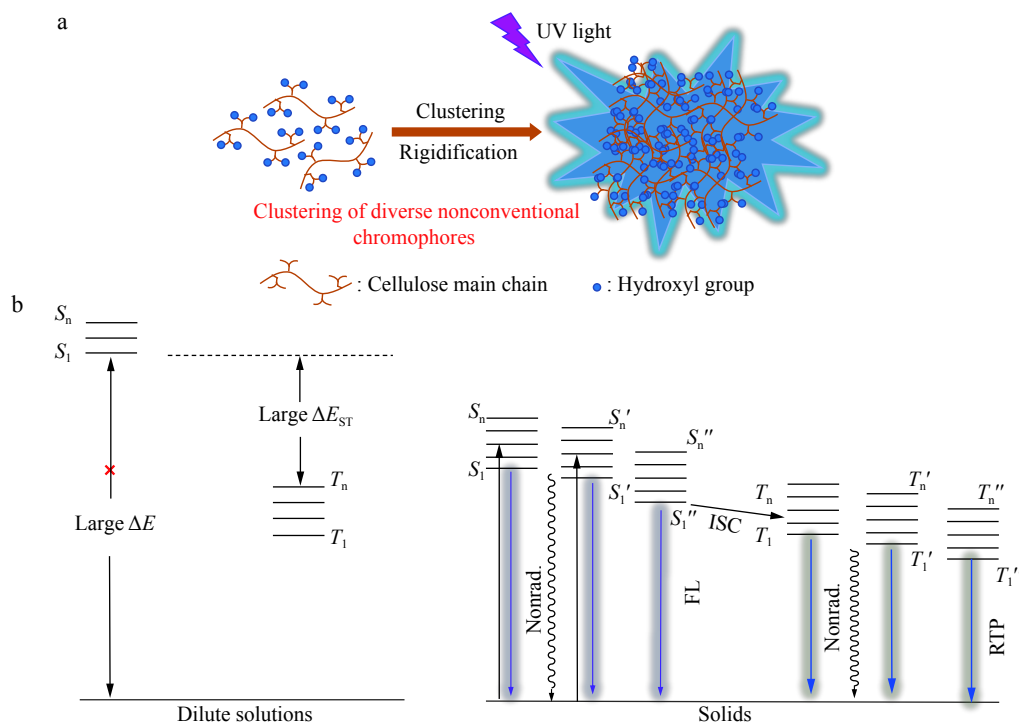


Fig. 6 Schematic illustration of (a) the emission mechanism and (b) RTP processes of CA and its derivatives

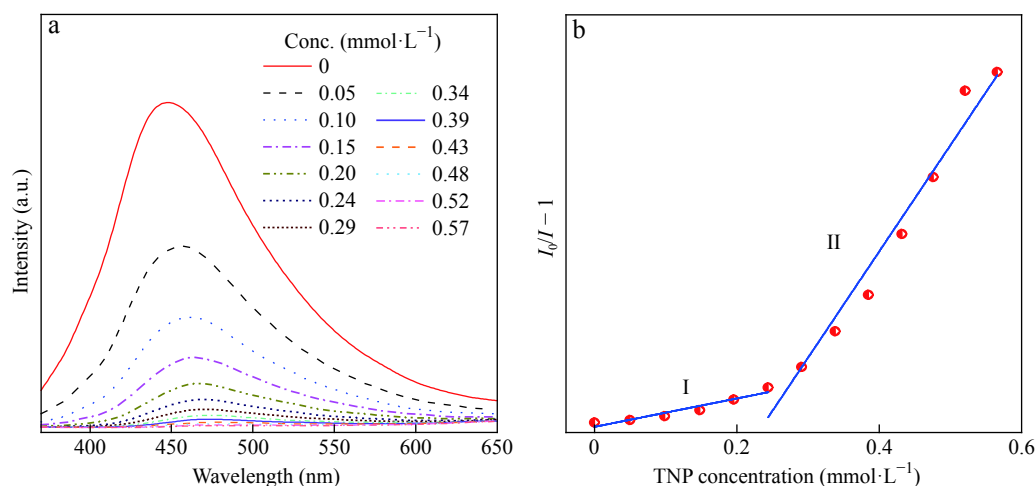


Fig. 7 (a) PL spectra of HEC aqueous solutions ($5 \text{ mg} \cdot \text{mL}^{-1}$) with different concentrations of TNP ($\lambda_{\text{ex}} = 350 \text{ nm}$); (b) Stern-Volmer plots of $I_0/I - 1$ (455 nm) against TNP concentrations in HEC solutions

CONCLUSIONS

In conclusion, we investigated the photophysical properties of MCC, HEC, HPC, and CA in different states. While MCC, HEC, and HPC showed bright emission and moreover unique RTP at solid states, CA displayed less intense solid emission without noticeable RTP. Such intrinsic emission could be well understood in terms of the CTE mechanism. In this scenario, clustering of ether, hydroxyl, and carbonyl units was responsible for the emission. Meanwhile, relatively weak emission of CA should be ascribed to its fewer hydrogen bonds and poor crystallinity. These results provide more information for the mechanism understanding of nonconventional luminogens, and moreover, shed new lights on the exploration of RTP from metal-free nonaromatic polymers. It is also believed that these common biomaterials could be further explored for emerging applications on account of their intrinsic emissions.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2215-2>.

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