Fluorescent linear CO_2-derived poly(hydroxyurethane) for cool white LED

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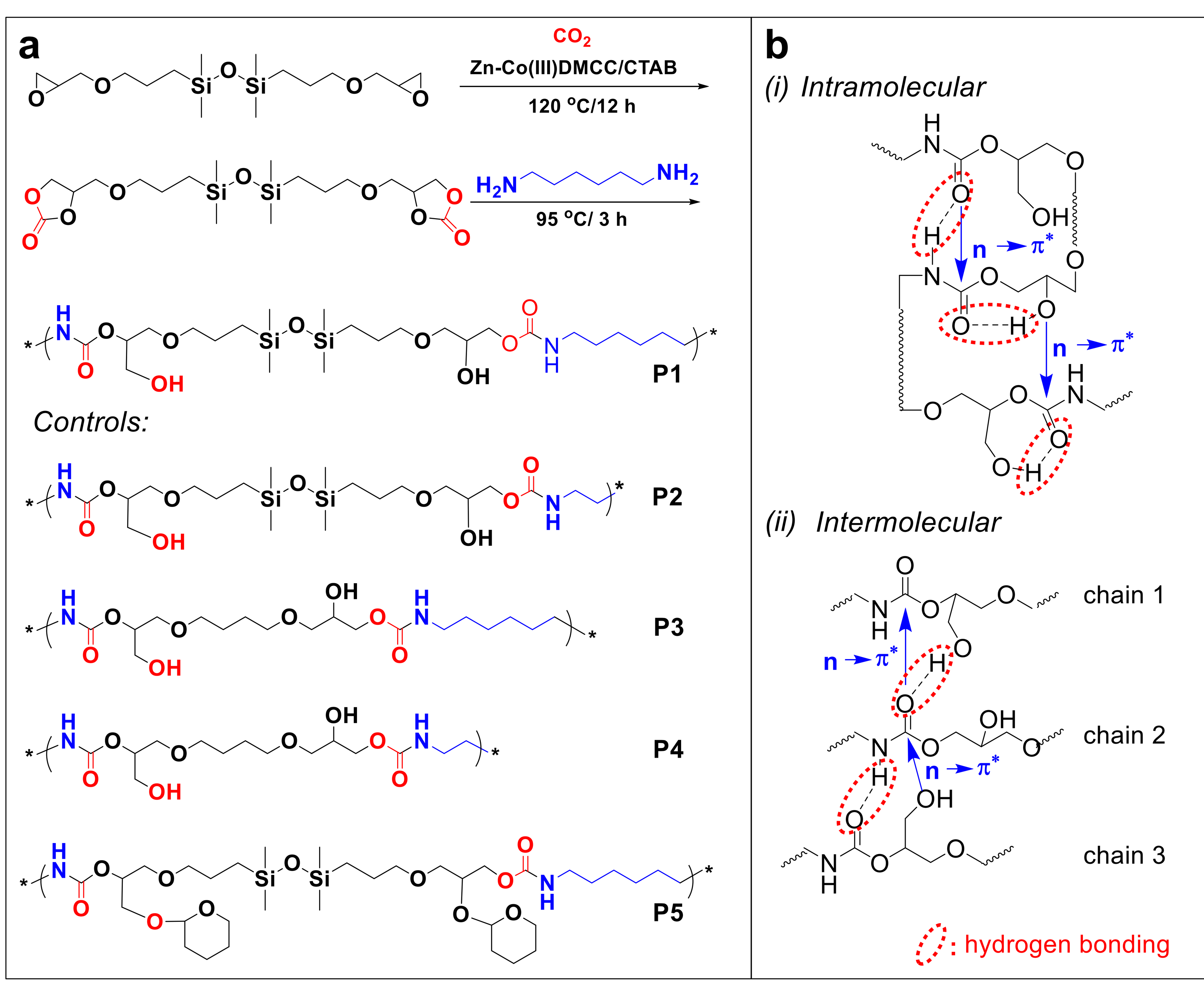
Abstract: The fluorescent properties of a linear poly(hydroxyurethane) (**P1**) from carbon dioxide (CO_2), siloxane (Si-O-Si)-containing bisepoxide and diamine are described. **P1** showed strong photoluminescence with a quantum yield of up to 23.6%, high photostability, broad absorption and emission spectra either in bulk or solution. The flexibility and hydrophobicity of the siloxane linkage in **P1** were utilized to drive the intense aggregation of hydroxyurethane chromophores combined with the hydrogen bonding interactions, leading to strong photoluminescence. **P1** was used as a single phosphor film for fabricating low-voltage cool white light-emitting diode device with competitive performances.

Introduction

Fluorescent materials, including inorganic materials, small organic molecules, macromolecules and nanostructured materials, are widely investigated because of their promising applications in display technology, electroluminescence, cell imaging and chemical sensors, etc. Presently, polymers with multiple carbonyl (C=O) moieties show blue luminescence. It is well established that aggregation-induced emission (AIE) is responsible for the PL property.

Herein, we report a linear siloxane (Si–O–Si)-containing poly(hydroxyurethane) (PHU, **P1**) that exhibited unprecedented strong fluorescent emission either in dilute solution or bulk. PHU was easy to prepare, and carbon dioxide (CO_2) was used as the source of the carbonyl groups via the reaction of CO_2, siloxane-containing bisepoxide and diamine in tandem (Scheme 1a). We also demonstrated that **P1** film could be used as a single phosphor for fabricating low-voltage cool white light-emitting diode (LED) with competitive performances.



Scheme 1. a) The syntheses of PHUs **P1**-**P5**. **P2**-**P5** were used as controls. b) Proposed mechanism of the blue emission for the PHUs.

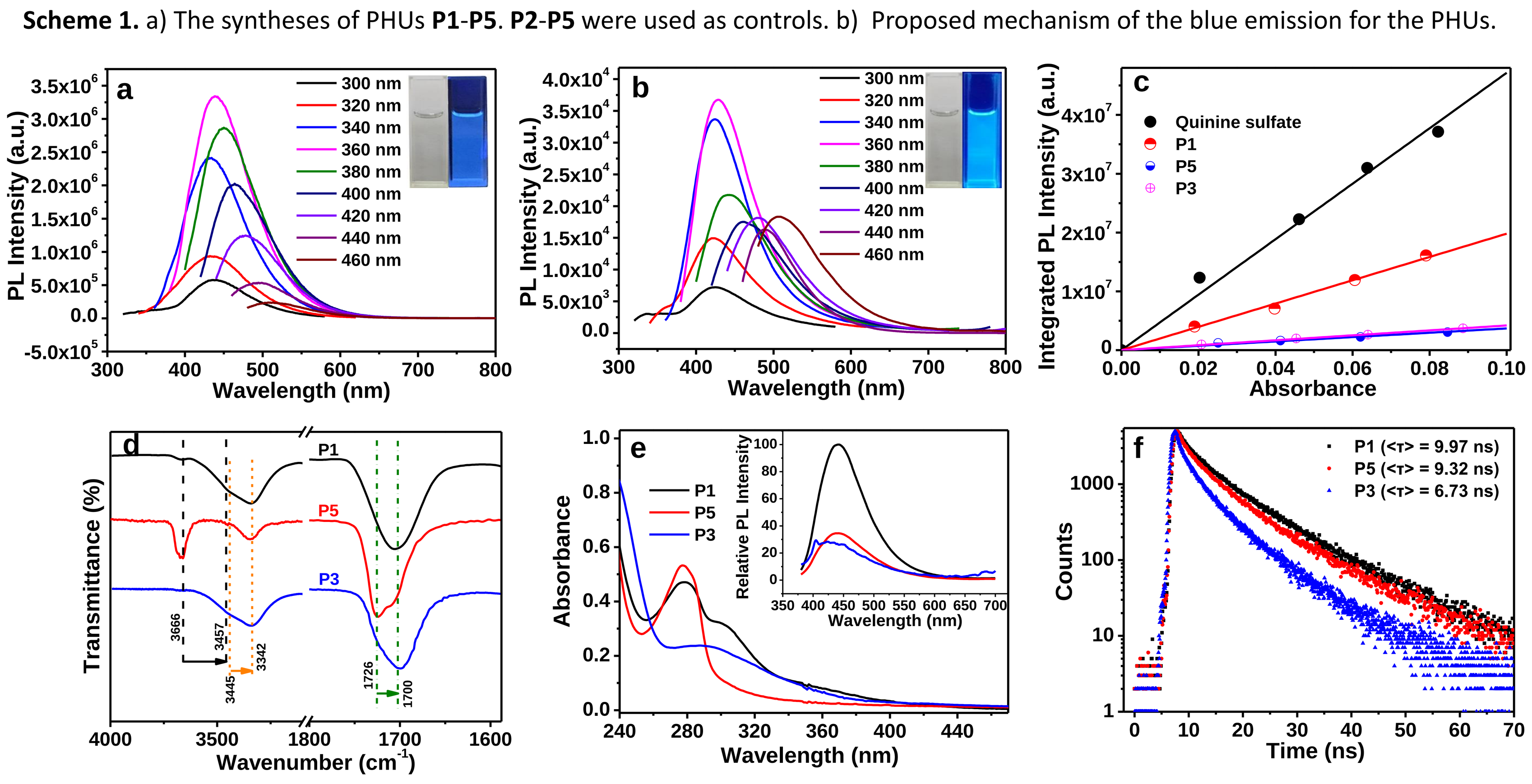


Fig. 1 (a, b) PL spectra of **P1** and **P3** at different excitation wavelengths in ethanol. Insert: photos of **P1** and **P3** in ethanol under daylight (left) and UV light (right, λ_{ex}=365 nm). (c) QY measurement of **P1**, **P3** and **P5** in ethanol. (d) FT-IR spectra of **P1**, **P3** and **P5**. (e) UV-vis absorption spectra of **P1**, **P3** and **P5** in ethanol. Insert: PL spectra of **P1**, **P3** and **P5** with equimolar hydroxyurethane unit in ethanol (λ_{ex} = 360 nm). (f) Time-resolved fluorescence decay curves for **P1**, **P3** and **P5** in ethanol (λ_{ex} = 375 nm).

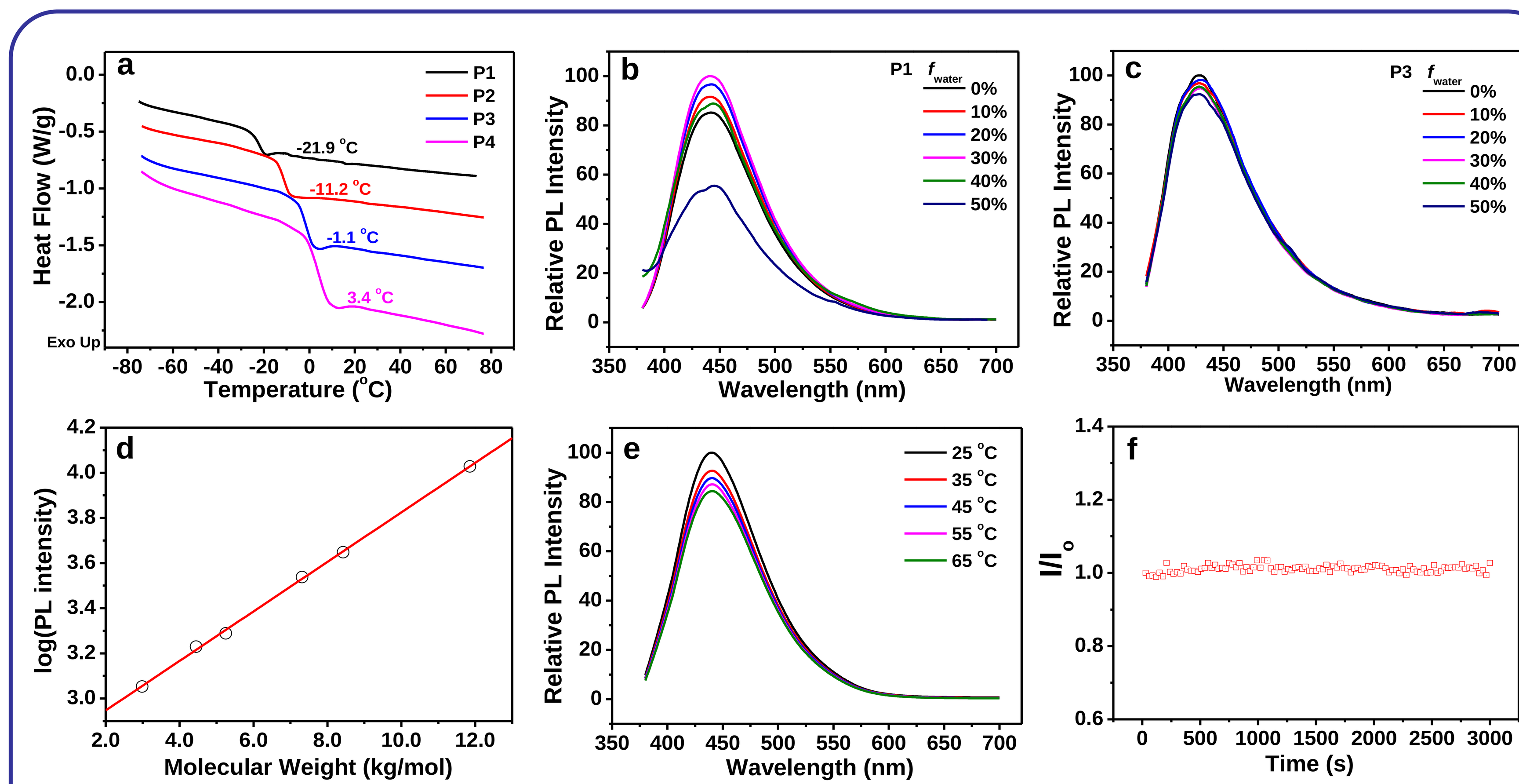


Fig. 2 (a) DSC curves of FPHUs (heating rate: 10°C/min, N_2 atmosphere). (b, c) PL spectra of **P1** and **P3** in ethanol/water solution with slowly increasing water fraction (f_{water}). (d) PL intensity (the logarithm of fluorescence intensity at 440 nm) of **P1** in ethanol with molecular weights, the solid line was the linear fit. (e) PL spectra of **P1** in ethanol at different temperatures. (f) The photostability of **P1** in ethanol.

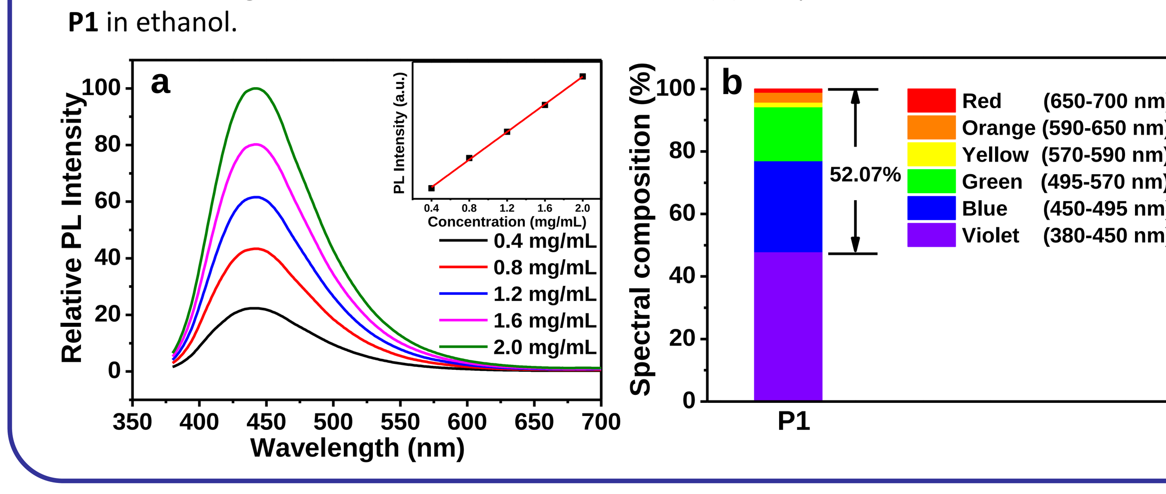


Fig. 3 (a) PL spectra of **P1** in ethanol at different concentrations. Insert: liner relationship of fluorescence intensity at 440 nm versus the concentrations of **P1**. (b) Blue-to-red spectral composition of the bulk **P1**.

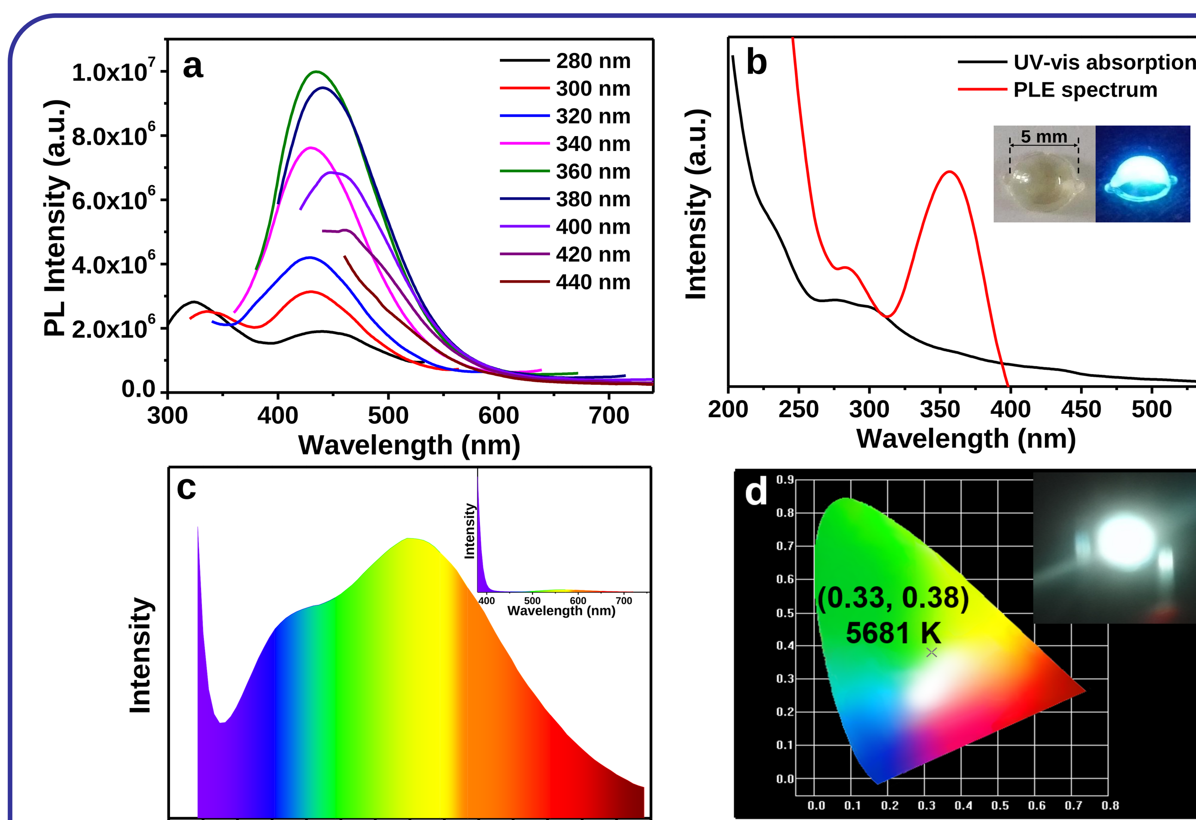


Fig. 4 (a) PL spectra of **P1** film. (b) UV–vis absorption, photoluminescence excitation of **P1** film. Inset: photos of **P1** film under daylight (left) and UV light (right, λ_{ex}=365 nm). (c,d) Emission spectra and CIE chromaticity coordinates of the WLED. Inserts: emission spectrum of the UV chip (c) and digital photo of the WLED under 3.6 V (d).

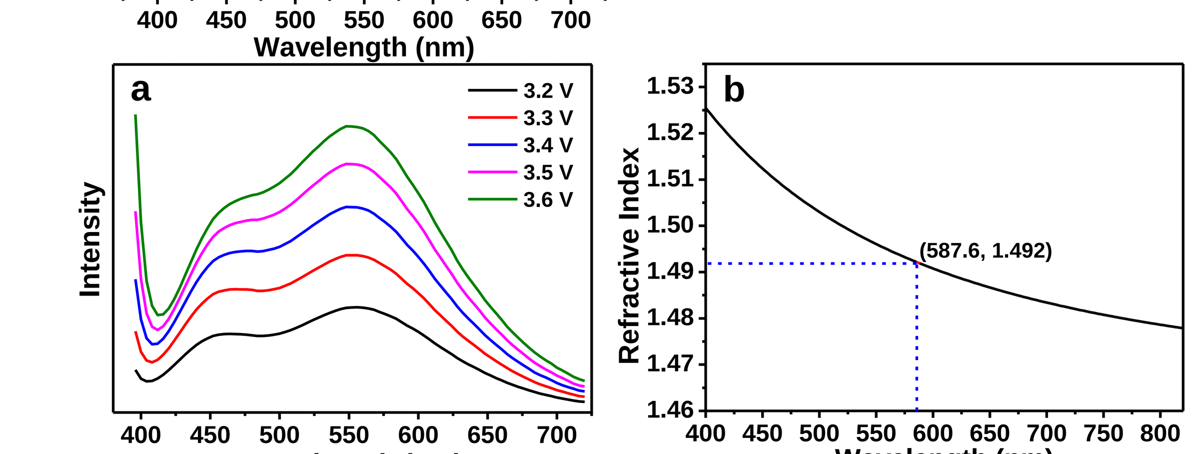


Fig. 5 (a) Emission spectra of the WLEDs under different working voltages. (b) The refractive index of **P1** via the wavelength from 400 to 800 nm (film thickness: 65.9 nm).

Conclusions

In summary, we developed a linear siloxane-containing PHU of which the carbonyl groups were derived from CO_2, exhibited strong fluorescence either in bulk or solution with high photostability, broad absorption and emission. The regulation of PL emission property could be achieved by precisely design or modification of their structure and chain conformation. We also demonstrated that **P1** could be used to fabricate white LED, which emitted cool white light at low voltage. The versatility of the large-scale synthesis and the ease to processing of linear PHUs make this new fluorescent material has a promising future. Our ongoing efforts are to seek a better understanding of the mechanism of this new chromophore and to develop PHUs with better fluorescence performance.

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