Perfectly Alternating and Regioselective Copolymerization of Carbonyl Sulfide and Epoxides via Metal-free Lewis Pairs

Fluorescent Linear CO_2-derived Poly(hydroxyurethane) for Cool White LED

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Abstract: The preparation of perfectly alternating and regioslective copolymers derived from the copolymerization of carbonyl sulfide (COS) and epoxides via metal-free Lewis pair catalysts composed of a Lewis base (amidine, guanidine, or quaternary onium salts) and a Lewis acid (triethyl borane) is described. Colorless and highly transparent copolymers of poly(monothiocarbonate) were successfully obtained with >99% tail-to-head content and high molecular weight (up to 92.5 kg/mol). In most instances, oxygen-sulfur exchange reactions (O/S ERs), which would generate random thiocarbonate and carbonate units, were effectively suppressed. The turnover frequencies (TOF) of these Lewis pairs catalyzed processes were as high as 119 h^{-1} at ambient temperature.

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

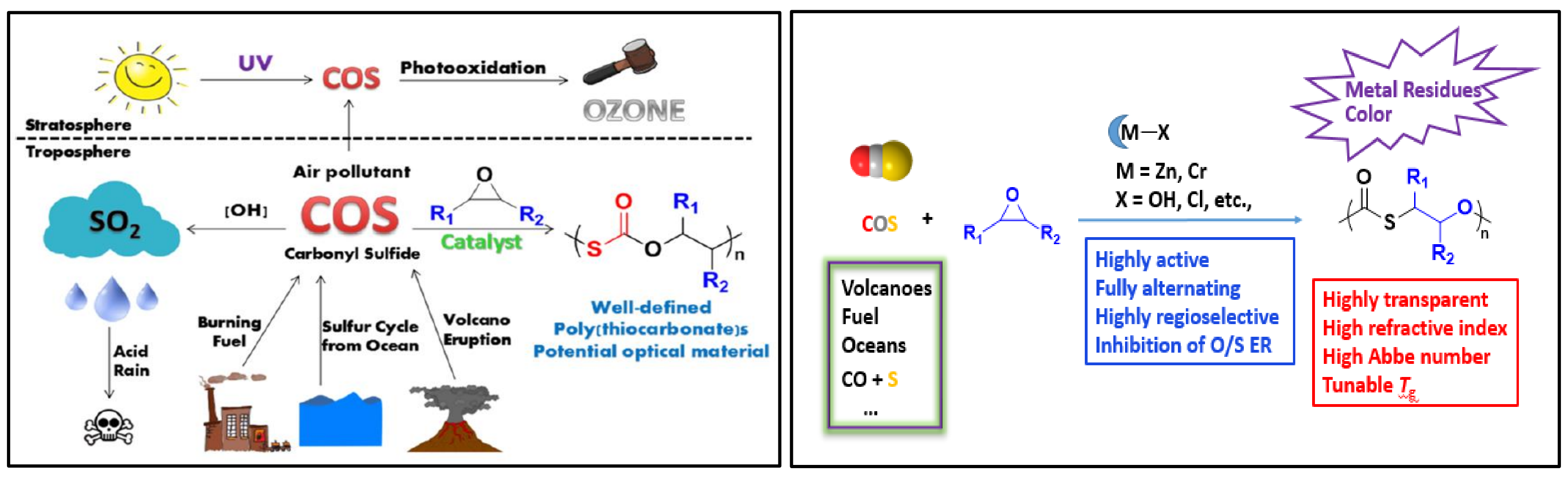

Fig. 1. Synthesis of poly(monothiocarbonate)s from COS/epoxide copolymerization (R_1 and R_2 represent substituted groups).

*C*arbonyl sulfide (COS) is a sulfur-containing one-carbon (C1) building block which is derived from the burning of fossil fuels, coal gas, and many chemical processes. However, the releasing of COS into the environment causes formation of sulfur aerosols, fog, haze, acid rain, as well as damage of the ozonosphere due to a series of photochemical processes. Concurrently, the utilization of COS can provide an atom-economic route upon copolymerization with epoxides to afford various functionalized copolymers. Presently, only metal catalysts have been shown to effectively promote the copolymerization of COS/epoxides, the residues of which impede the applications of these copolymers

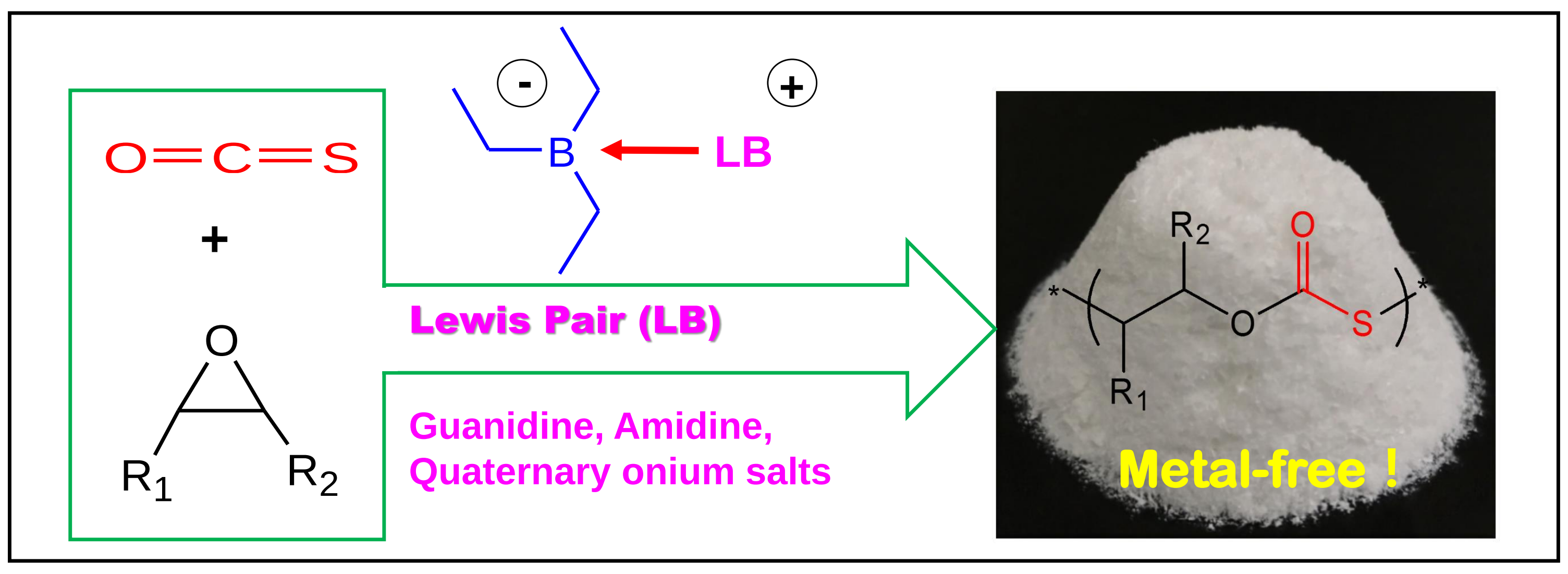

Fig. 2. poly(monothiocarbonate)s from the copolymerization of COS with epoxides meditated by metal-free catalyst.

Active Lewis pairs for copolymerization

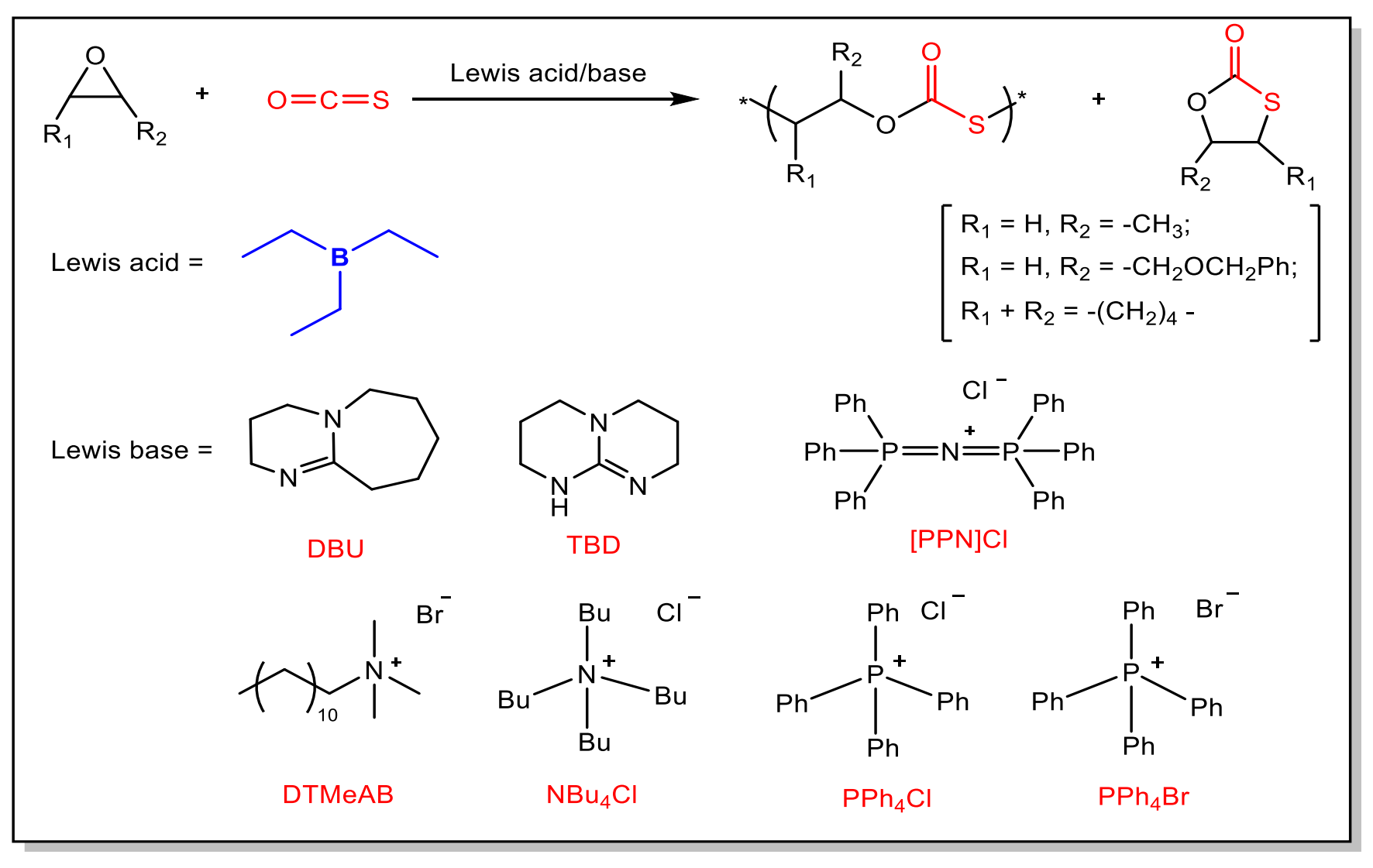

Fig. 3. Active Lewis pairs for the copolymerization of COS with epoxides.

TEB: triethylborane;

DBU: 1,5-diazabicyclo[5.4.0]undec-5-ene;

TBD: 1,5,7-Triazabicyclododecene;

[PPN]Cl: Bis(triphenylphosphine)iminium chloride;

DTMeAB: Dodecyltrimethylammonium bromide;

NBu_4Cl: Tetrabutylammonium chloride;

PPh_4Cl: Tetraphenyl phosphonium chloride;

PPh_4Br: Tetraphenyl phosphonium bromide;

*C*onsidering the similarity of Frustrated Lewis Pairs (FLPs) and binary metal/base catalyst systems, we developed a fully alternating and perfectly regioselective COS/epoxide copolymerization process catalyzed by the Lewis pair of TEB with various Lewis bases, including amidine, quinidine, quaternary onium salts to provide colorless and highly transparent well-defined poly(monothiocarbonate)s.

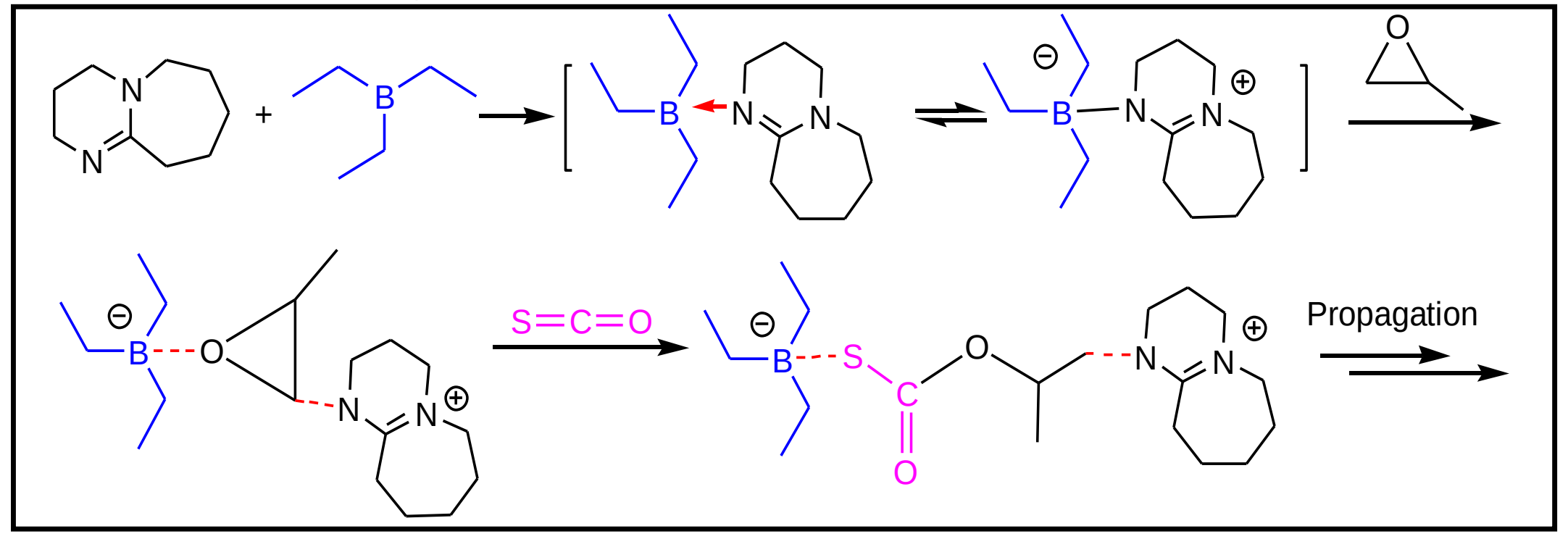

Fig. 4. The formation of intramolecular TEB/DBU pair for activating COS and PO.

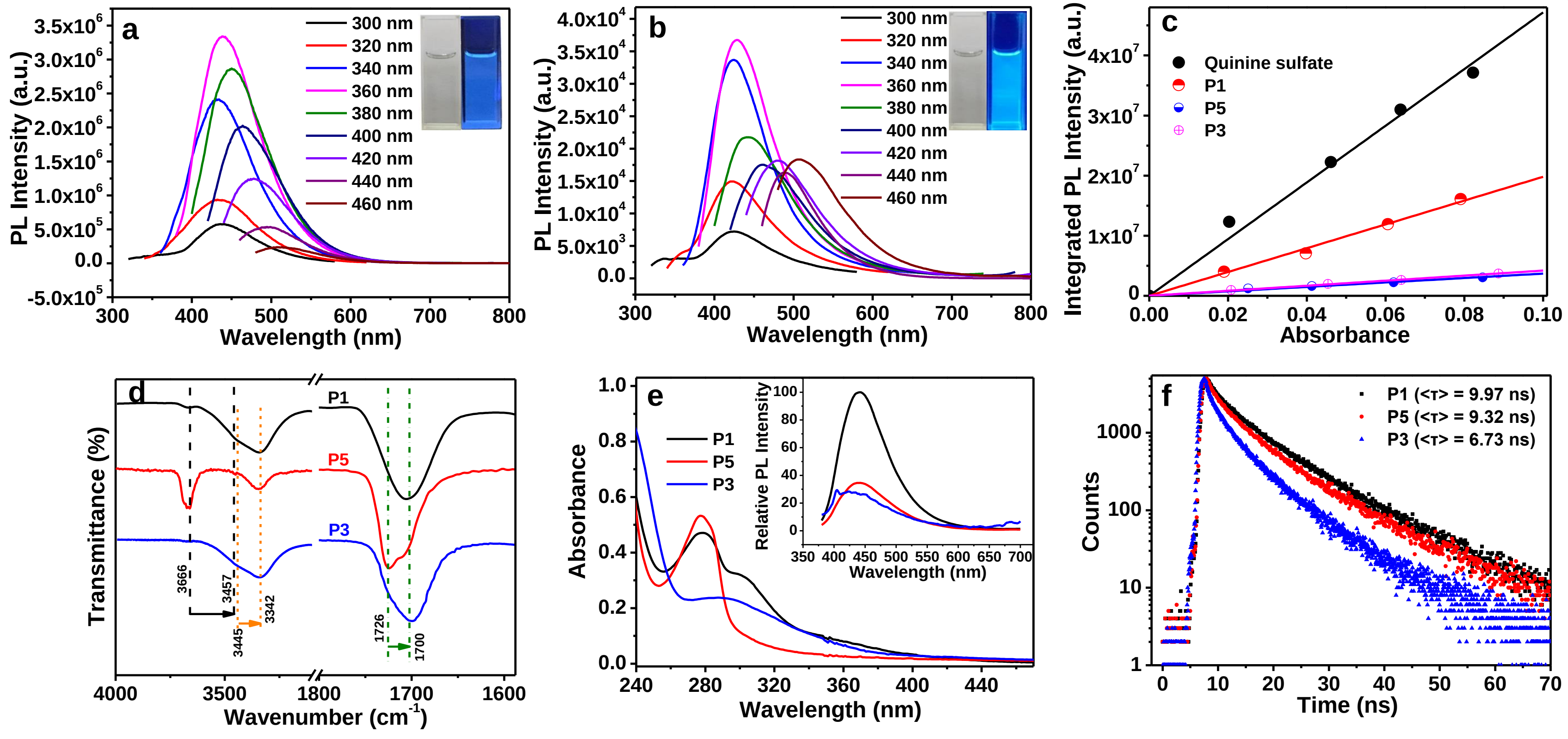

Fig. 1 (a, b) PL spectra of **P1** and **P3** at different excitation wavelengths in ethanol. Insert: photos of **P1** and **P3** in ethanol under daylight (left) and UV light (right, λ_{ex}=365 nm). (c) QY measurement of **P1**, **P3** and **P5** in ethanol. (d) FT-IR spectra of **P1**, **P3** and **P5**. (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).

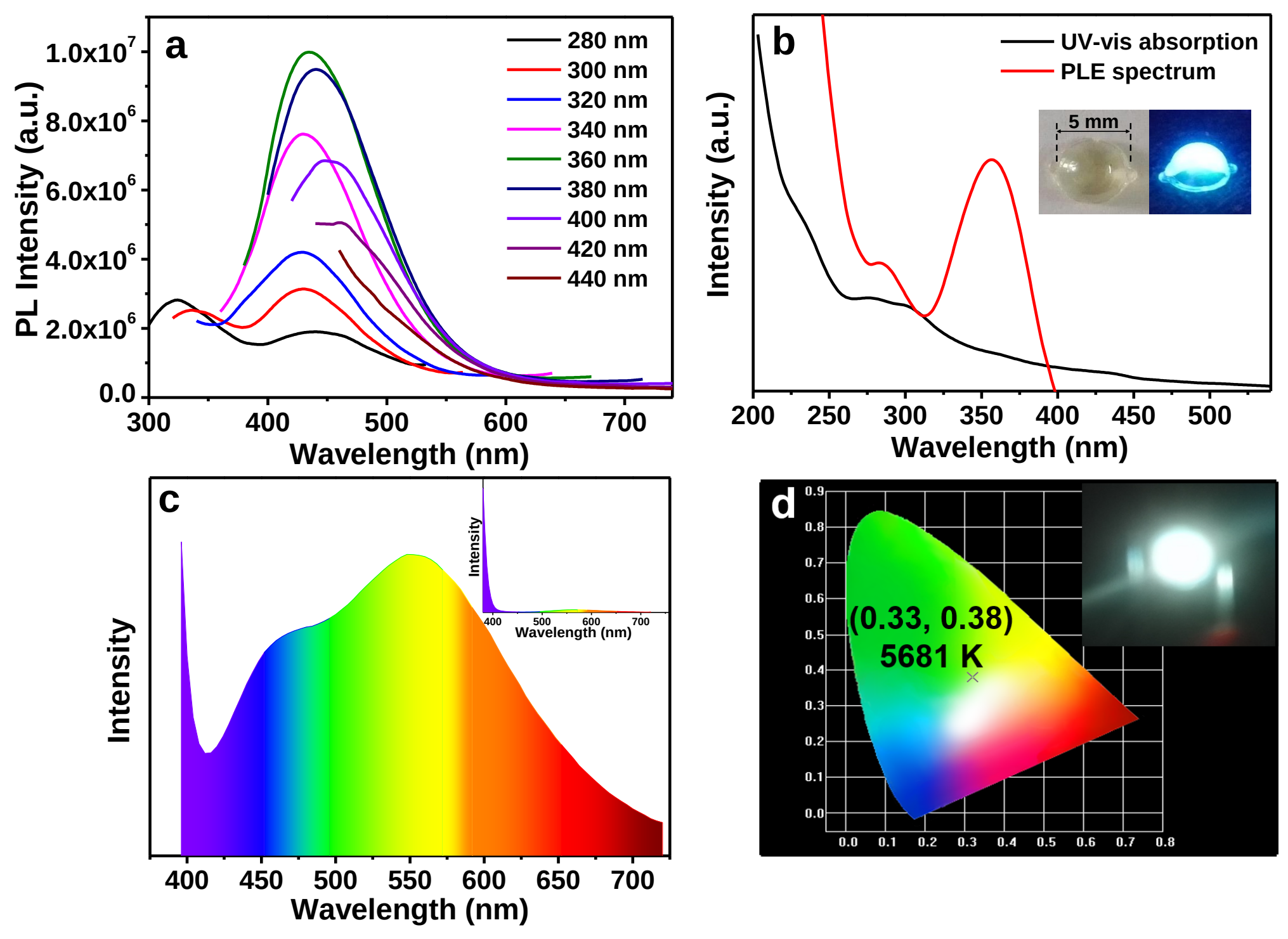

Fig. 2 (a) PL spectra of **P1** film. (b) UV–vis absorption, photoluminescence excitation of **P1** film. Inset: photos of **P1** film under daylight (left) and UV light (right, λ_{ex}=365 nm). (c,d) Emission spectra and CIE chromaticity coordinates of the WLED. Inserts: emission spectrum of the UV chip (c) and digital photo of the WLED under 3.6 V (d).

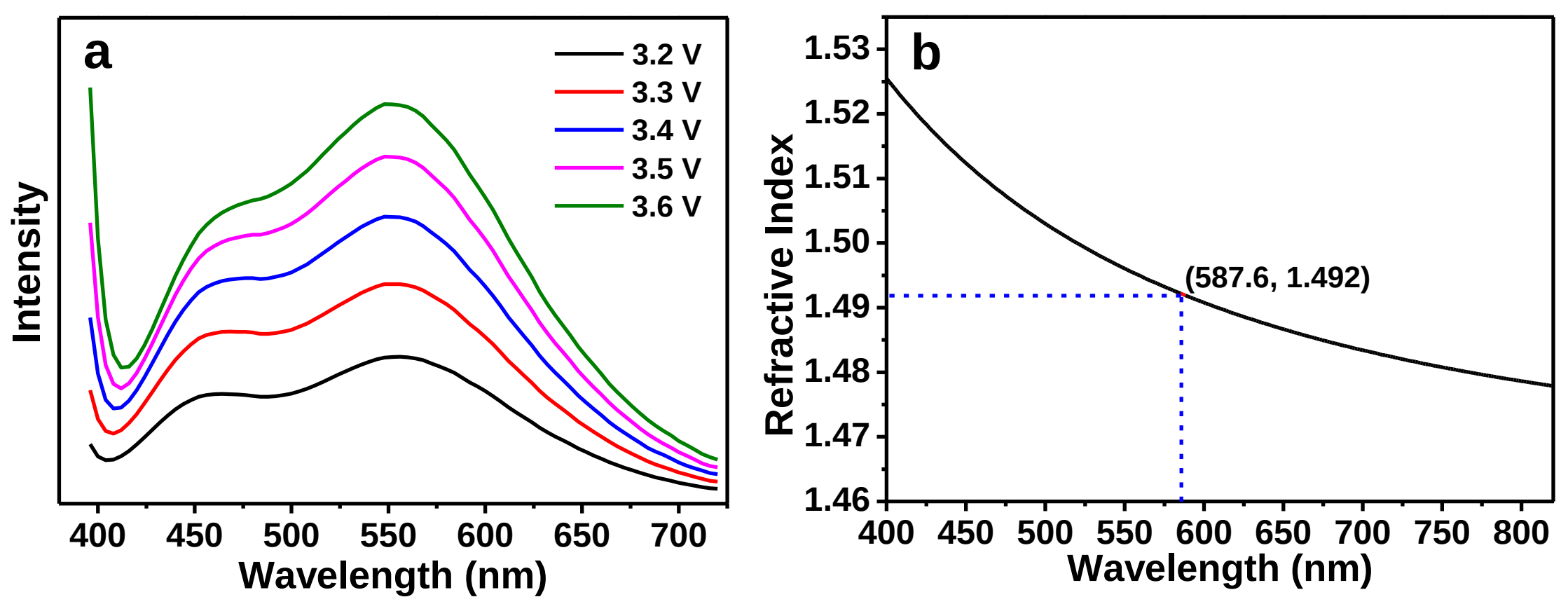

Fig. 3 (a) Emission spectra of the WLEDs under different working voltages. (b) The refractive index of **P1** via the wavelength from 400 to 800 nm (film thickness: 65.9 nm).

Acknowledgement

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References

[1] Yang J L, Wu H L, Li Y, et al. Perfectly Alternating and Regioselective Copolymerization of Carbonyl Sulfide and Epoxides by Metal-Free Lewis Pairs[J]. Angewandte Chemie, 2017, 56(21):5774.

[2] Luo, M.; Zhang, X.-H.; Darensbourg, D. J. Accounts of Chemical Research 2016, 49, 2209.

[3] Liu B, Wang Y L, Bai W, et al. Fluorescent linear CO 2-derived poly (hydroxyurethane) for cool white LED[J]. Journal of Materials Chemistry C, 2017, 5(20): 4892.