Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

A fluorescein-centered polymer as a phosphor for fabricating pure white light-emitting diodes

Bin Liu,[a] Han-Yi Duan,[a] Ya-Ling Wang,[c] Bin-Yang Du,[a] Qing Yang,[d] Jun-Ting Xu,[a] Yong-Zhen Yang,[c] Andreas Greiner [b] and Xing-Hong Zhang *[a]

[a] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China
[b] Macromolecular Chemistry, Bavarian Polymer Institute, University of Bayreuth, Universitatsstraße 30, 95440 Bayreuth, Germany
[c] MOE Key Laboratory of Interface Science and Engineering in Advanced Materials, Research Center on Advanced Materials Science and Technology, Taiyuan University of Technology, Taiyuan 030024, P. R. China
[d] State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, Zhejiang University, Hangzhou 310027, China

Experimental

Materials

Fluorescein (95%, J&K), 2-Bromoisobutyryl bromide (98%, Sigma-Aldrich), 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA) (98%, J&K), Copper(I) bromide (CuBr) (98%, J&K), triethylamine (99.5%, Aladdin), 4-dimethylaminopyridine (DMAP) (99%, Aladdin) and dry dimethyl sulfoxide (99.7%, J&K) were used as received. Methyl acrylate (MA) (99.5%, Aladdin) and 2-hydroxyethyl acrylate (HEA) (97%, J&K) were filtered through basic alumina to remove the inhibitor. (2-oxo-1,3-dioxolane-4-yl)methyl methacrylate (DOMA) was synthesized as our previous report.[1] Tetrahydrofuran (THF) was distilled before use. The fluorescein 2-bromoisobutyrate was synthesized according to the reported method.[2]

Characterization

^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Advance DMX 400 MHz and 101 MHz spectrometer by using TMS as internal reference, respectively. Gel permeation chromatography (GPC) with RI (Waters 2414) detection system was carried out at 60°C with DMF as the eluent at a flow rate of 1.0 mL min^{-1}. UV-vis spectra were obtained in the range of 200–800 nm at 1 nm scan interval with a scan speed of 600 nm min^{-1} by a Cary 100 Scan UV-vis spectrophotometer (America). The excitation and emission spectra were collected on a Horiba Fluoromax-4 luminescence spectrometer using a Xe lamp as an excitation source. And all of the PL spectra of polymers were tested repeatedly at least 3 times. Absolute quantum yield (QY) measurements were performed with a calibrated integrating sphere on a QM40-LS spectrophotometer. The fluorescence decay curve was recorded based on EDINBURGH FLS980 transient fluorescence & phosphorescence spectrograph. The multidimensional time-correlated single photon counting (TCSPC) method was employed to estimate the fluorescence decay lifetime. The Spectra Scan PR 655 was applied to analyze the spectra, CIE coordinates, correlated color temperature and color rendering index (CRI) of the white LEDs.

Synthesis of fluorescein 2-bromoisobutyrate (Flu-Br)

A clean, dry round bottom flask containing fluorescein (2.0 g, 5.98 mmol), DMAP (73.0 mg), triethylamine (2.98 mL) and THF (100 mL) was cooled to 0 ^{o}C in ice-water bath. 2-Bromoisobutyryl bromide (2.66 mL) mixed with THF (30 mL) was added dropwise to the flask. The flask was then removed from the ice-water bath and the reaction was allowed to proceed for 24 h at room temperature. During this period, the reaction mixture slowly changed from brown to yellow. THF was removed completely under reduced pressure and dichloromethane was then added to dissolve the mixture. The reaction mixture was washed successively with saturated $NaHCO_3$ aqueous solution (four times), dilute HCl (twice), saturated NaCl aqueous solution (twice). The organic layer was dried over mixture of anhydrous $MgSO_4$ overnight and passed through a silica gel column using methanol/dichloromethane (1:20) as eluent before the solvent was removed in vacuo. The structure was verified by ^{1}H and ^{13}C NMR spectroscopy. Yield: 70.7%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (s, 1H), 7.81 (d, J = 26.0 Hz, 1H), 7.43 (s, 1H), 7.34 (s, 2H), 6.99 (s, 2H), 2.05 (s, 18H). ^{13}C NMR (101 MHz, DMSO) δ 169.26, 168.42, 152.26, 151.81, 150.81, 136.11, 130.66, 129.51, 125.28, 125.13, 124.11, 117.94, 116.71, 110.01, 80.77, 56.81, 29.95.

Synthesis of poly(2-oxo-1,3-dioxolane-4-yl) methyl methacrylate (P1) using Flu-Br as initiator

CuBr (3.0 mg, 0.02 mmol), Flu-Br (1.5 mg, 0.0024 mmol), DMSO (1.5 mL) and DOMA (1.5 mL) were added to a clean, oven dried Schlenk tube, along with a magnetic follower. The Schlenk tube was degassed by three freeze-pump-thaw cycles and sealed with a rubber septum under nitrogen atmosphere. PMDETA (5.0 µL, 0.024 mmol) was added to the tube via a degassed syringe. Three freeze-pump-thaw cycles were then carried out using liquid nitrogen. The tube was placed in an oil bath at 25 °C for 2 minutes. The reaction mixture was quenched by exposure to oxygen and passed through a silica gel column to remove copper salts. The polymer solution was purified by precipitation in excess methanol three times and then dried at 60 °C under vacuum to a constant weight. Yield: 20.7%.

Synthesis of poly(2-hydroxyethyl acrylate) (P2) using Flu-Br as initiator

CuBr (3.4 mg, 0.024 mmol), Flu-Br (5.0 mg), DMSO (2.5 mL) and HEA (2.5 mL) were added to a clean, oven dried Schlenk tube, along with a magnetic follower. The Schlenk tube was degassed by three freeze-pump-thaw cycles and sealed with a rubber septum under nitrogen atmosphere. PMDETA (6.0 µL, 0.029 mmol) was added to the tube via a degassed syringe. Three freeze-pump-thaw cycles were then carried out using liquid nitrogen. The tube was placed in an oil bath at 50 °C for 4 h. The reaction mixture was quenched by exposure to oxygen and purified by dialysis against deionized water in a dialysis tube with molecular weight cutoff (MWCO) of 3500 at room temperature for 3 days to remove HEA, copper salts and DMSO. The water was removed by freeze-drying of the sample. Insoluble sample, no yield was determined.

Synthesis of poly(methyl acrylate) (P3) using Flu-Br as initiator

CuBr (3.4 mg, 0.024 mmol), Flu-Br (5.0 mg), DMSO (2.5 mL) and MA (2.5 mL) were added to a clean, oven dried Schlenk tube, along with a magnetic follower. The Schlenk tube was degassed by three freeze-pump-thaw cycles and sealed with a rubber septum under nitrogen atmosphere. PMDETA (6.0 µL, 0.029 mmol) was added to the tube via a degassed syringe. Three freeze-pump-thaw cycles were then carried out using liquid nitrogen. The tube was placed in an oil bath at 50 °C for 2 h. The reaction mixture was quenched by exposure to oxygen and passed through a silica gel column to remove copper salts. The polymer solution was purified by precipitation in excess methanol three times and then dried at 60 °C under vacuum to a constant weight. Yield: 35.1%.

The blends of fluorescein with PDOMA (from free radical polymerization of DOMA using AIBN as the initiator)

Fluorescein (2.6 mg), PDOMA (750.0 mg) (M_n=101.8 kg/mol) and DMF (20 mL) were added to a round bottom flask along with a magnetic follower for 4 h at room temperature. DMF was removed completely under reduced pressure under 60 °C. Then grind the blends into powder in a mortar.

The blends of Flu-Br with PDOMA (from free radical polymerization of DOMA using AIBN as the initiator)

Flu-Br (5.0 mg), PDOMA (750.0 mg) (M_n=101.8 kg/mol) and DMF (20 mL) were added to a round bottom flask along with a magnetic follower for 4 h at room temperature. DMF was removed completely under reduced pressure under 60 °C. Then grind the blends into powder in a mortar.

Fabrication of the tunable yellow-to-white LEDs

For the fabrication of tunable yellow-to-white LEDs, InGaN based blue LED chip (λ_{em}= 420 or 460 nm) was selected. A certain concentration of **P1**/DMF (or **P3**/DMF) solution was added into cup-shaped optical lens and put it into air-circulating oven at 80 °C for 5 h to remove the solvent. Finally, the optical lens was firmly fixed on the LED chip to accomplish the fabrication of LEDs. Unlike **P1** and **P3,** a certain amount of **P2** was added directly into the cup-shaped optical lens and thermal treated at 80 °C for 5 h. All of the LEDs were tested repeatedly at least 3 times.

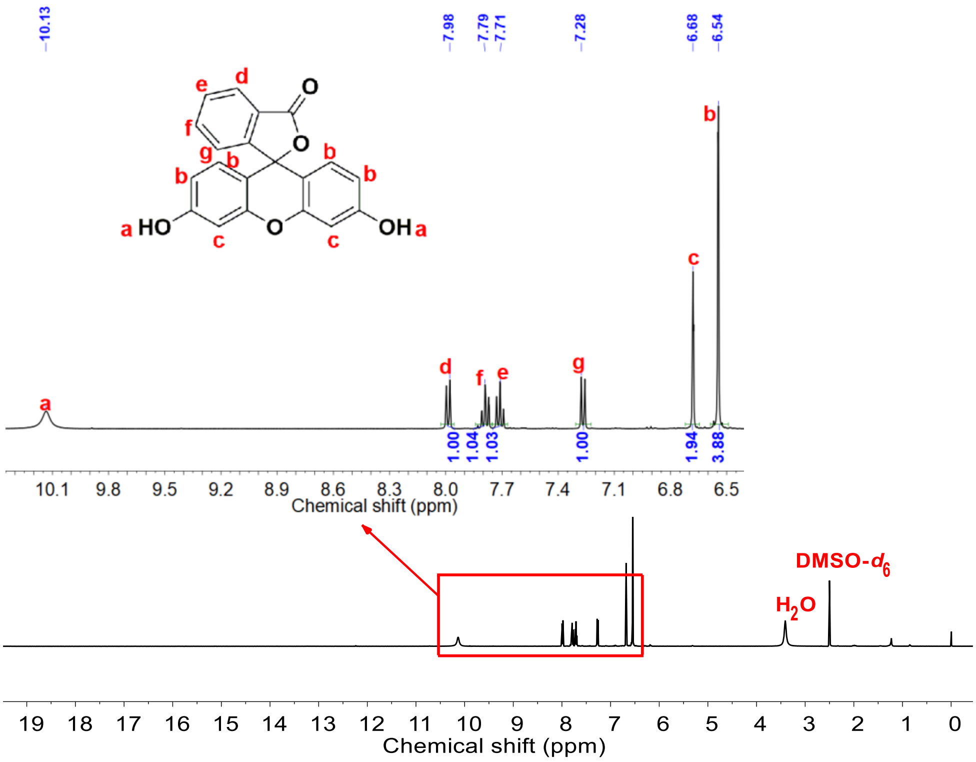

Figure S1. ^{1}H NMR spectrum of fluorescein (400 MHz, DMSO-d_6).

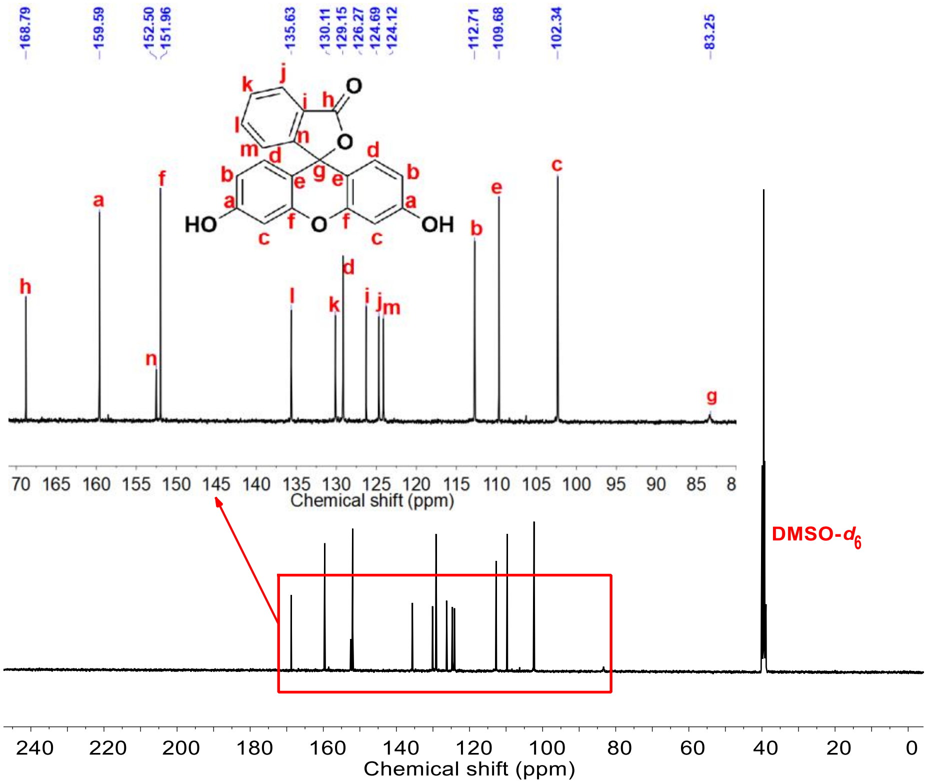

Figure S2. ^{13}C NMR spectrum of fluorescein (101 MHz, DMSO-d_6).

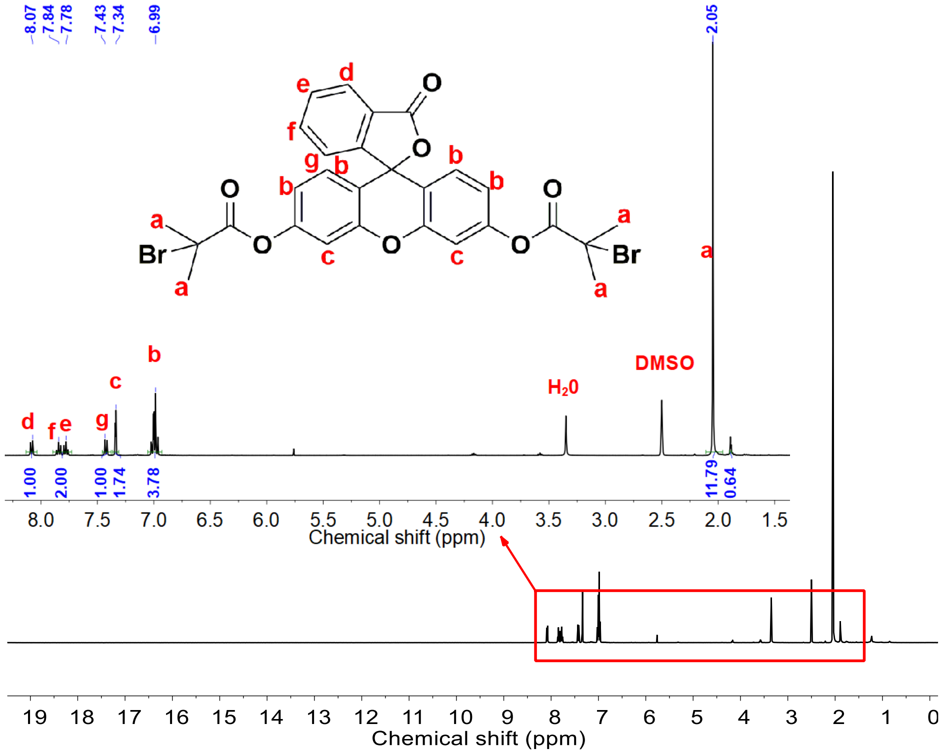

Figure S3. ^1H NMR spectrum of Flu-Br (400 MHz, DMSO-d_6).

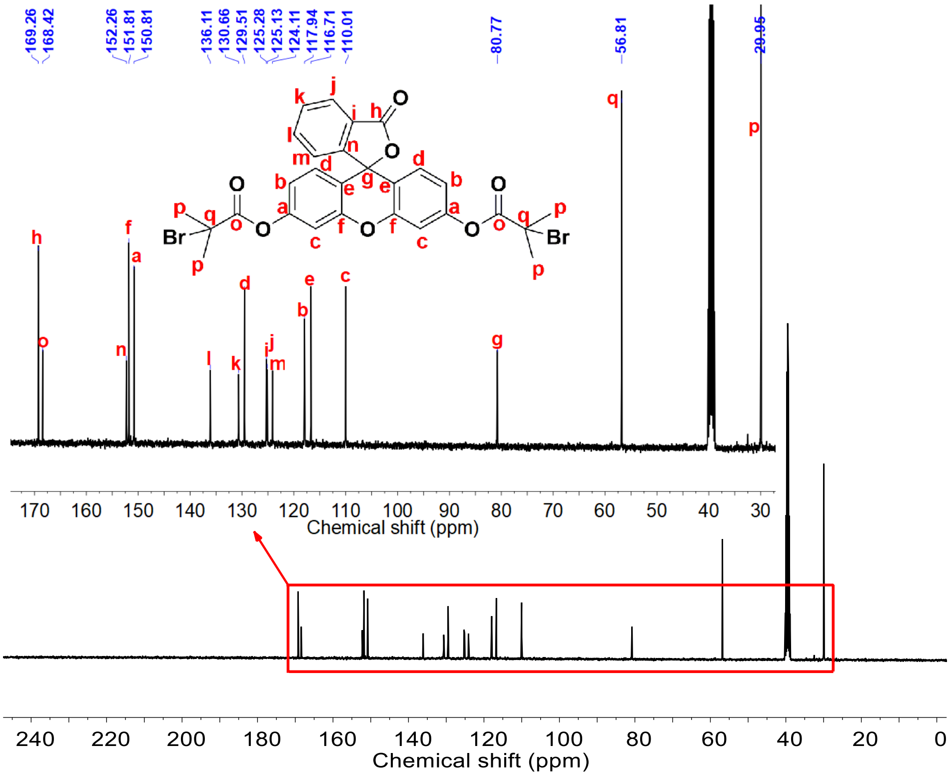

Figure S4. ^{13}C NMR spectrum of Flu-Br (101 MHz, DMSO-d_6).

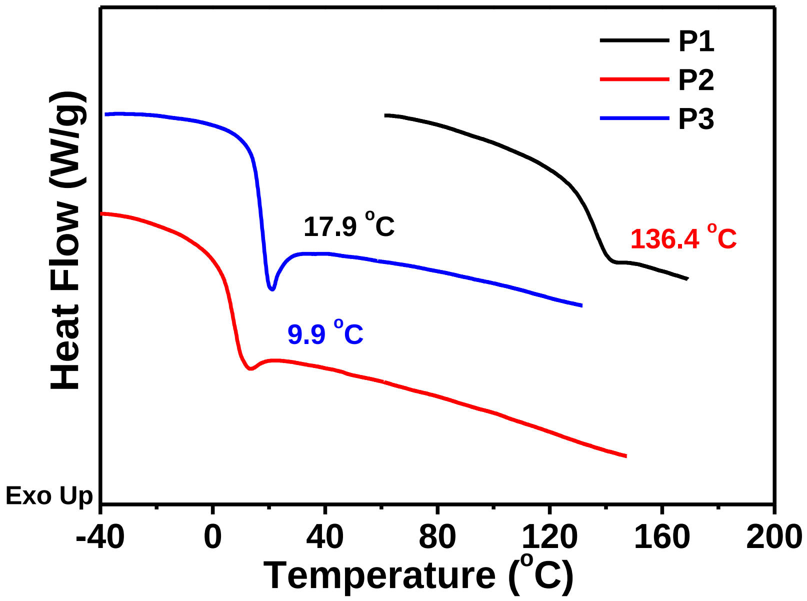

Figure S5. DSC curves of polymers (heating rate: 10 °C min^{-1}, N_2 atmosphere).

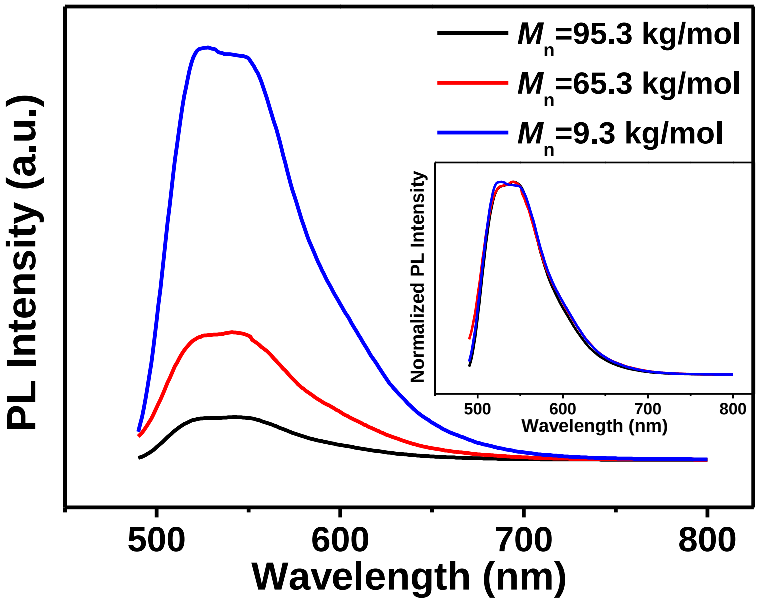

Figure S6. PL spectra of **P1** with different molecular weights in solid state.

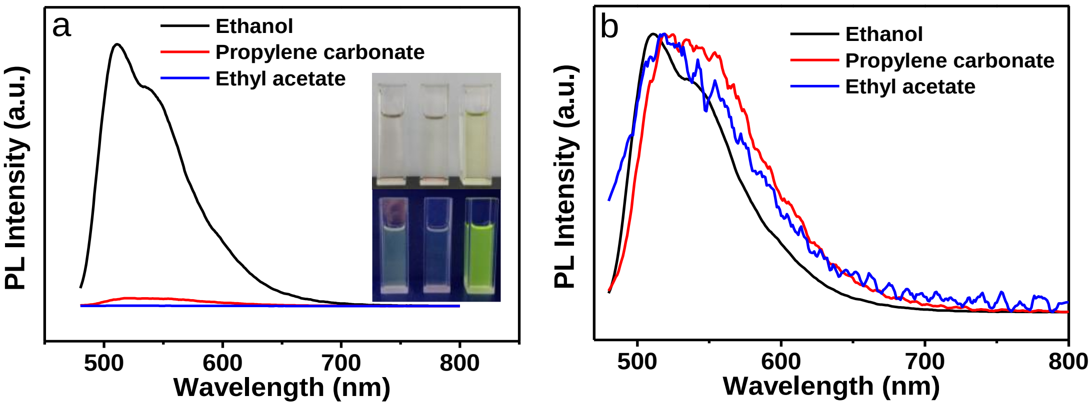

Figure S7. (a) PL spectra of fluorescein in different solvents with the same concentration (0.1 mg/mL) (λ_{ex}= 460 nm). Insert: photos of under daylight (above) and UV light (below) (λ_{ex}= 365 nm) (from left to right: PC, EA and ethanol). (b) The normalized PL spectra of fluorescein in different solvents with the same concentration (0.1 mg/mL) (λ_{ex}= 460 nm).

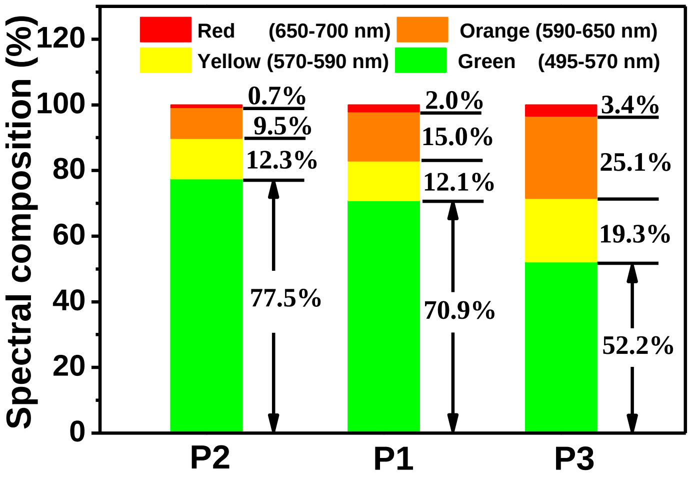

Figure S8. Green-to-red spectral composition of the polymers.

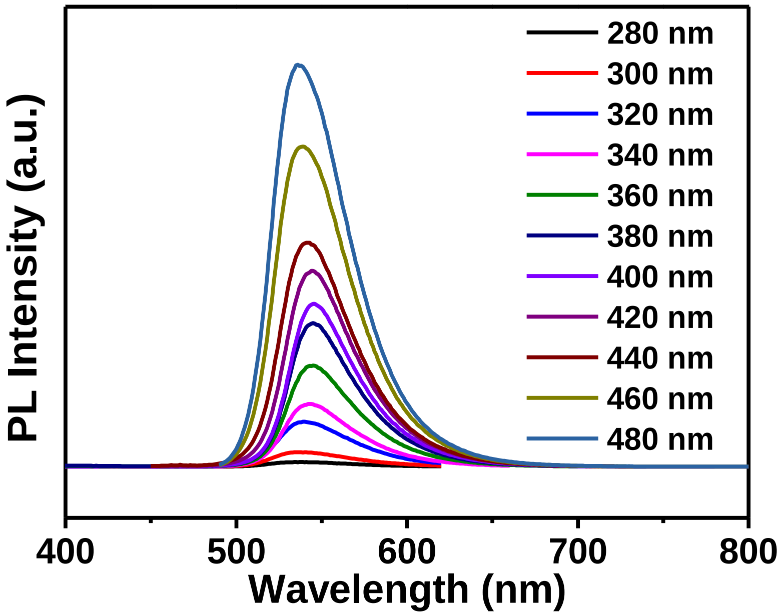

Figure S9. PL spectra of **P2** at different excitation wavelengths in solid state.

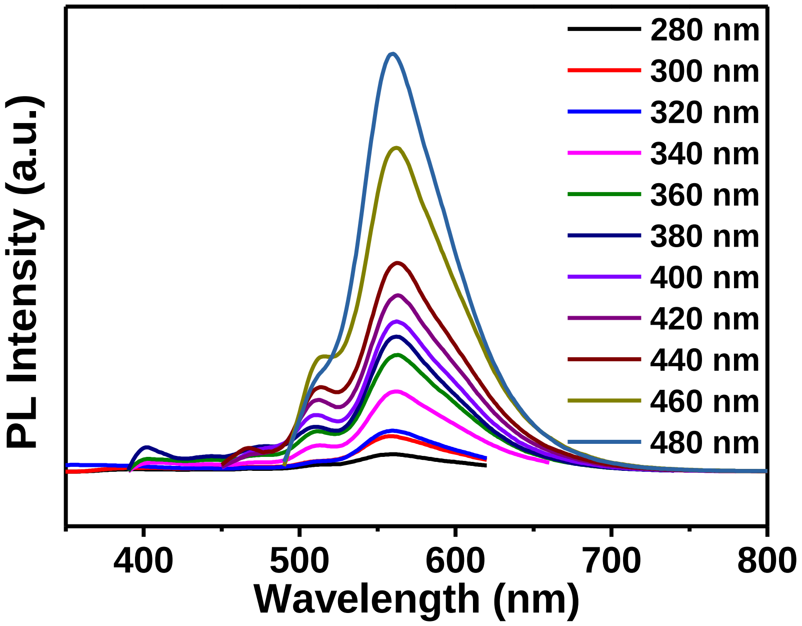

Figure S10. PL spectra of **P3** at different excitation wavelengths in solid state.

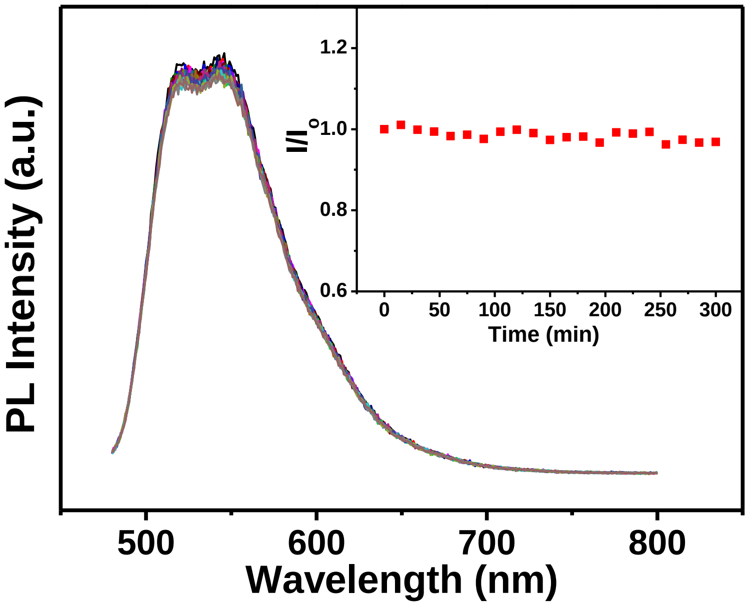

Figure S11. The photostability of **P1** in solid state every fifteen minutes.

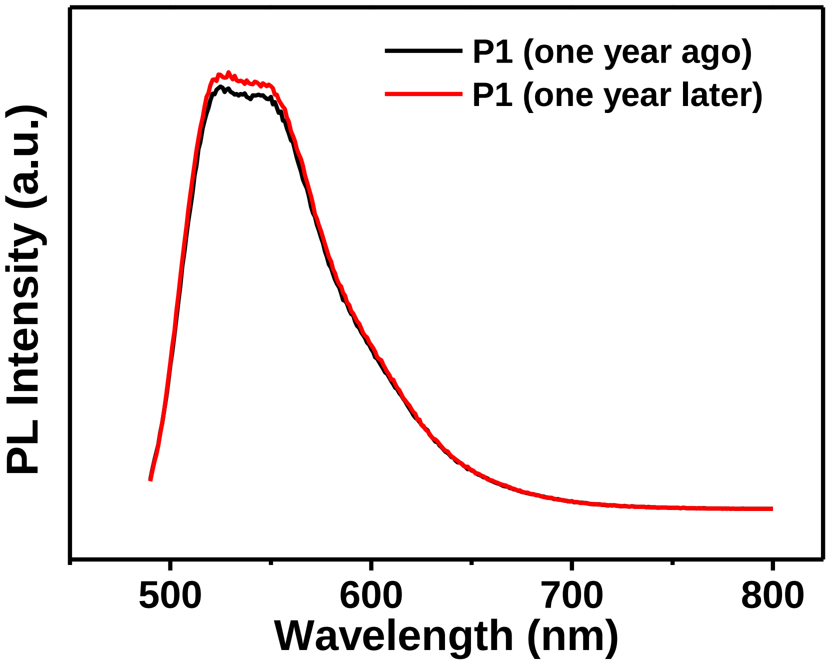

Figure S12. PL spectra of **P1** in solid state one year ago and one year later (λ_{ex}= 460 nm), showing the repeatability of the performances.

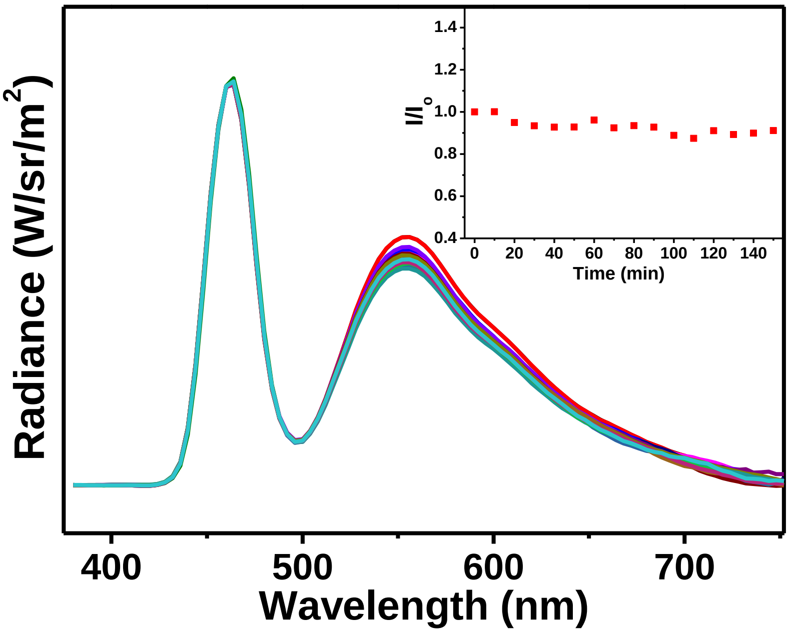

Figure S13. The stability of pure white LEDs prepared from **P1** and 460 nm blue LED chip every ten minutes.

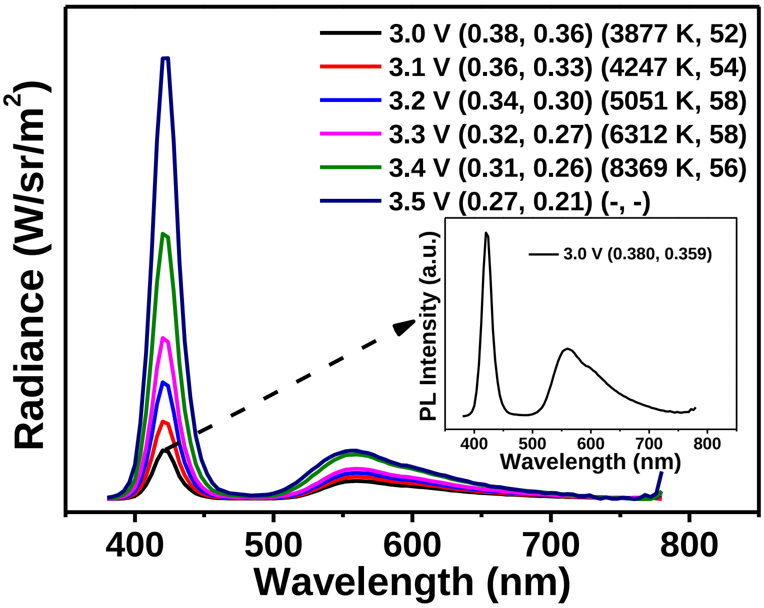

Figure S14. Electroluminescence spectra of **P1** under different working voltages (420 nm blue LED chip).

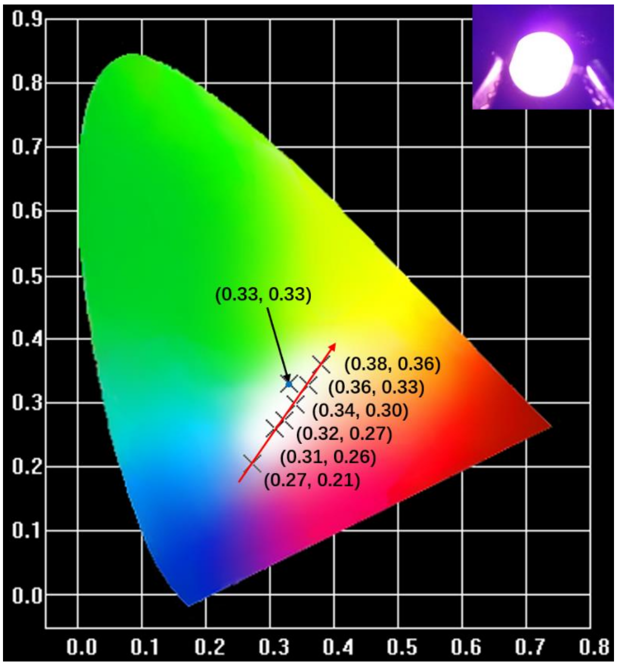

Figure S15. CIE chromaticity coordinates of the white LEDs for **P1** (420 nm blue LED chip).

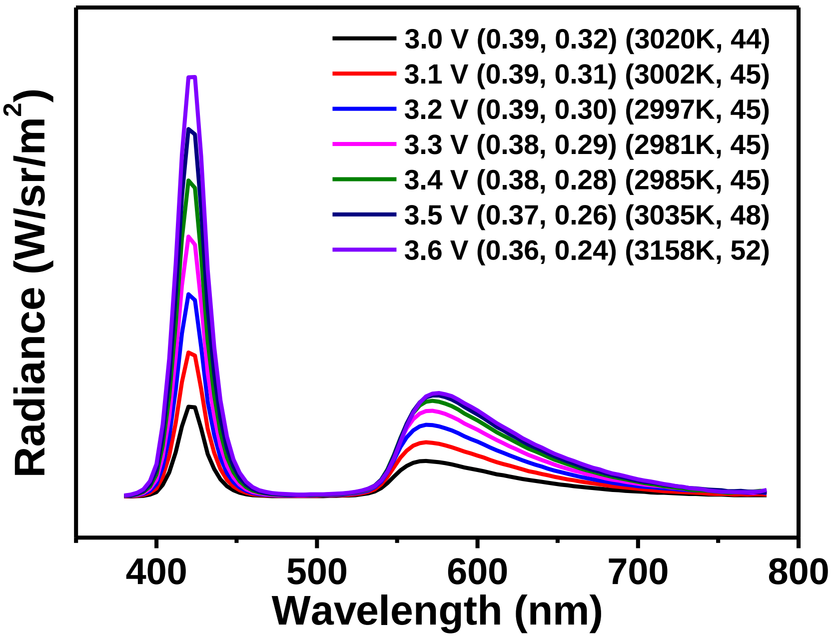

Figure S16. Electroluminescence spectra of **P2** under different working voltages (420 nm blue LED chip).

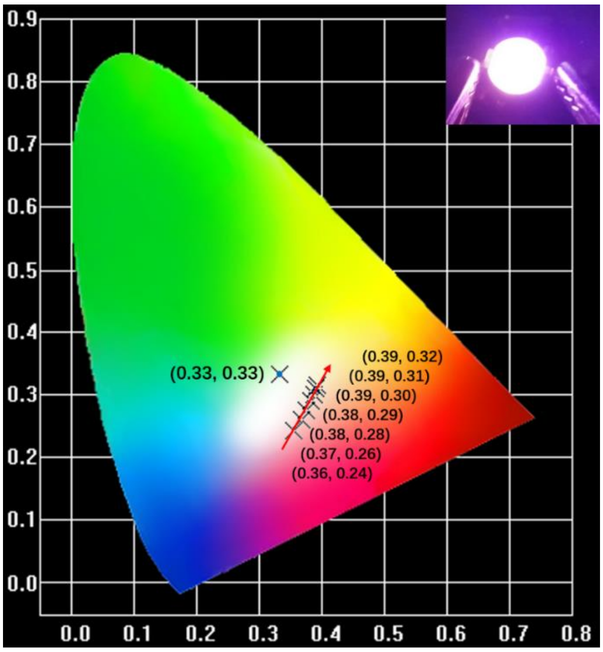

Figure S17. CIE chromaticity coordinates of the white LEDs for **P2** (420 nm blue LED chip).

References

1 B. Liu, Y. Y. Zhang, X. H. Zhang, B. Y. Du and Z. Q. Fan, *Polym. Chem.*, 2016, **7**, 3731.

2 N. Haridharan, K. Ponnusamy and R. Dhamodharan, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5329.