Rapid preparation of highly transparent piezoresistive balls for optoelectronic devices

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Experimental section

Materials

Choline chloride (ChCl) and acrylic acid (AA) were purchased from Macklin. The poly(ethylene glycol) diacrylate (PEG), 2-Hydroxy-2-methylpropiophenone (photoinitiator 1173), and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (photoinitiator, TPO) were received from Shanghai Aladdin Reagent. The Shanghai KPT company (China) provided the electroluminescent ZnS:Cu powders (D417).

Preparation of piezoresistive balls

The preparation of polymerizable deep eutectic solvents (PDESs) followed our previously published method:[1] the dried ChCl and AA were mixed at a 1: 2 molar ratio and a homogenous solution was formed after heating and stirring at 90 °C for around 3h. The photoinitiator 1173 and TPO were mixed in a weight ratio of 1:1. Next, PDESs (20g), photoinitiator (2-5 wt %) and crosslinker PEG (1.0-2.5 wt %) were mixed and stirred under 50 °C for 25 min. The poly(PDES) were acquired as the typical procedure: the mixture was taken up into a 1 ml syringe, of which the horizontal distance from the UV light source (power: 3000w, Zhongshan Youwei Printing Equipment Co., Ltd) was 17 cm and the vertical distance was 16 cm; the mixture was ejected at a constant velocity of 0.33 mL s^{-1} from the syringe which was equipped with 20G injection head and polymerized via photo-induced free radical polymerization; simultaneously, the substrate pulled out at a speed of 16 cm s^{-1}. The poly(PDES) are designated as PxCy, which represents x wt % photoinitiator and y wt % crosslinker.

Preparation of optoelectronic devices

There were four layers for the optoelectronic devices, bottom to top, in order, conductive glass, emissive layer, piezoresistive balls and nonconductive glass. The emissive layer was prepared following the published method.[2] The weight ratio of Dow Corning SYLGARD 184 liquid to ZnS:Cu microparticles was 1:1.

The mixture was spin-coated at a speed of 1000 r/s for 60s and solidified for 2h at 80 °C. The power device that enabled input power to be transferred from DC to AC, was purchased from the Shanghai KPT company.

Characterization

^{1}H NMR spectra were carried out on a 600 MHz Bruker AVANCE III NMR spectrometer. Chloroform was used as external reference. The Fourier transform infrared (FTIR) was recorded and the wavenumber range from 2000 to 1000 cm^{-1} using a Bruker Vertex 33 spectrometer. Differential scanning calorimetry (DSC) was carried out on a 214 Polyma NETZSCH tester under a nitrogen atmosphere. The PDESs were heated at 10 °C min^{-1}, and the temperature range was from -150 to 90 °C. Mechanical compression and cycle were carried out on an Instron 5565. The compression process of transparent piezoresistive ball (diameter of 2 mm) was recorded by a Nikon Digital Sight DS-Fil camera, and the diameter of the piezoresistive ball in the recorded photograph was analyzed by ruler tool of Photoshop. The optical transmittance was recorded by the UV−vis spectrometer (Cary60, USA). The conductivity of samples was recorded using an electrochemical workstation (CHI660E) and the frequency range used was from 0.01 to 10^{5} Hz. The resistance variations of piezoresistive balls were tested by a digital graphical sampling multimeter (DMM7510, Keithley, USA). The two- and three-dimensional figures for schematic illustration were drawn by Adobe Illustrator and 3D Studio Max, respectively. In addition, the Adobe Illustrator was used to combine pictures.

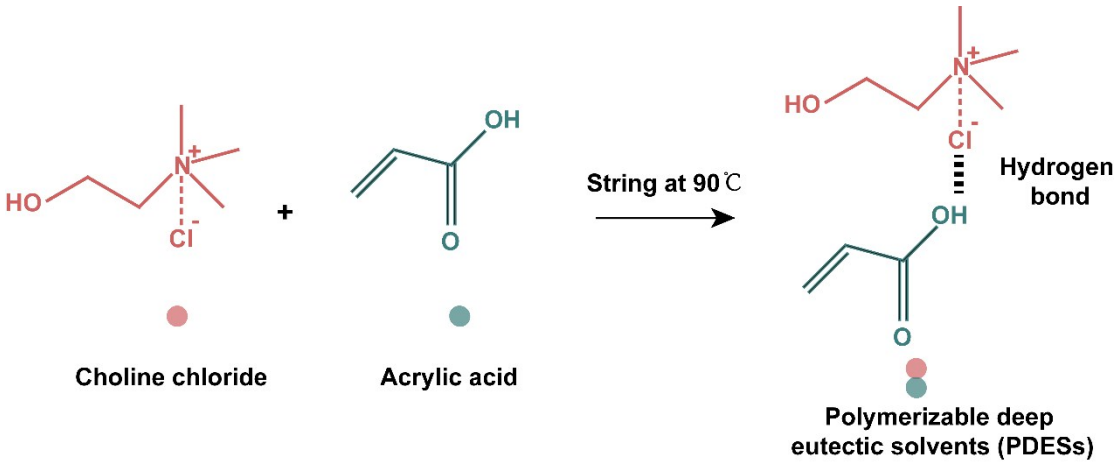

Fig. S1 The preparation of polymerizable deep eutectic solvents (PDESs) that followed our previously published method.[1]

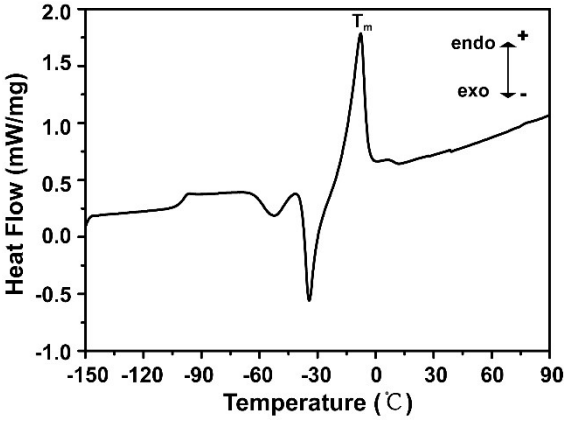

Fig. S2 DSC trace of PDESs.

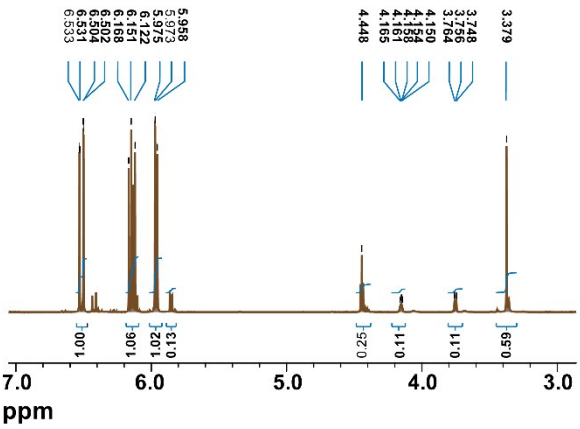

Fig. S3 Nuclear magnetic resonance spectra of PDESs.

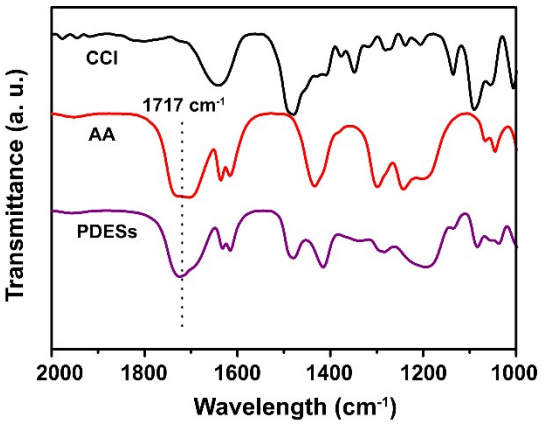

Fig. S4 Fourier transform infrared spectra of choline chloride (ChCl), acrylic acid (AA), and PDESs.

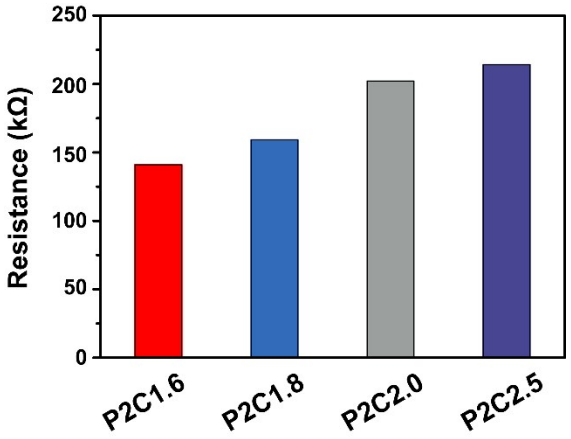

Fig. S5 The resistance of a series of transparent balls.

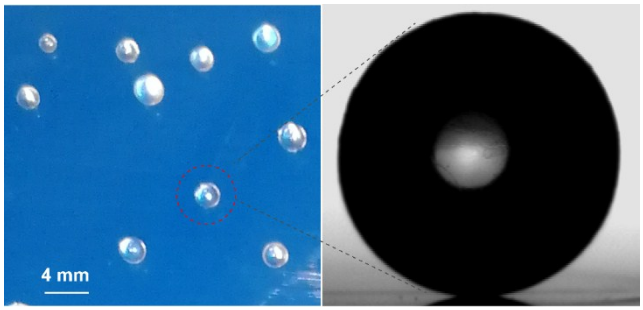

Fig. S6 Macroscopic features of transparent balls with 2 wt % photoinitiator and 1.6 wt % crosslinker.

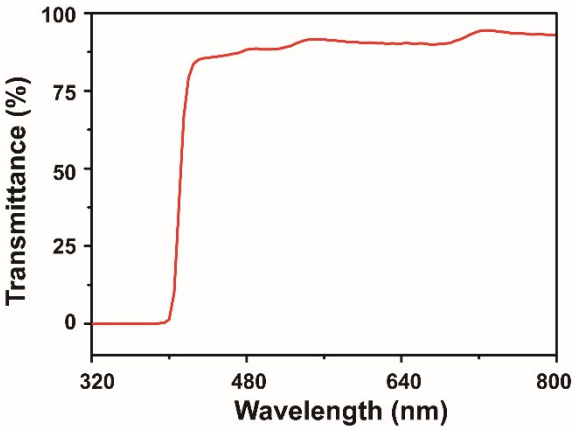

Fig. S7 Optical property (2 mm thickness) of poly(PDES) with 2 wt % photoinitiator and 1.6 wt % crosslinker. The PDES was spread onto a laboratory-made mould, of which from bottom to top are, in order, the glass sheet, release film, 2 mm rubber spacer, release film and glass sheet. After, the preparation of the poly(PDES) film was similar to that of transparent balls. The mould exposed to strong UV light for 3s and the distance of mould from the UV light source was 17 cm.

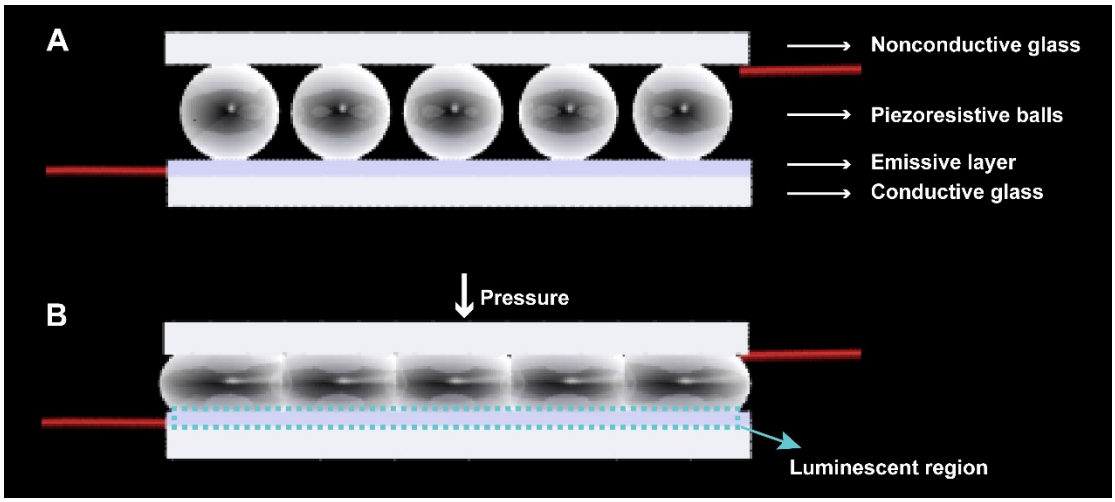

Fig. S8 Piezoresistive balls based optoelectronic devices in the (A) off and (B) on working states.

The optoelectronic device is in the off state (Fig. S8A), and the piezoresistive ball connects with electrode by providing pressure (Fig. S8B). When applying high frequency alternating voltage and providing pressure, the optoelectronic devices will emit a blue luminescent light. ZnS doped with Cu creates luminescent center, and optoelectronic devices emit a blue luminescent light due to the higher contribution from blue centers (the deepest energy levels) at high electrical frequencies.[3, 4] Noticeably, the luminescent region only appeared when the emissive layer is sandwiched between piezoresistive ball and conductive glass.[5]

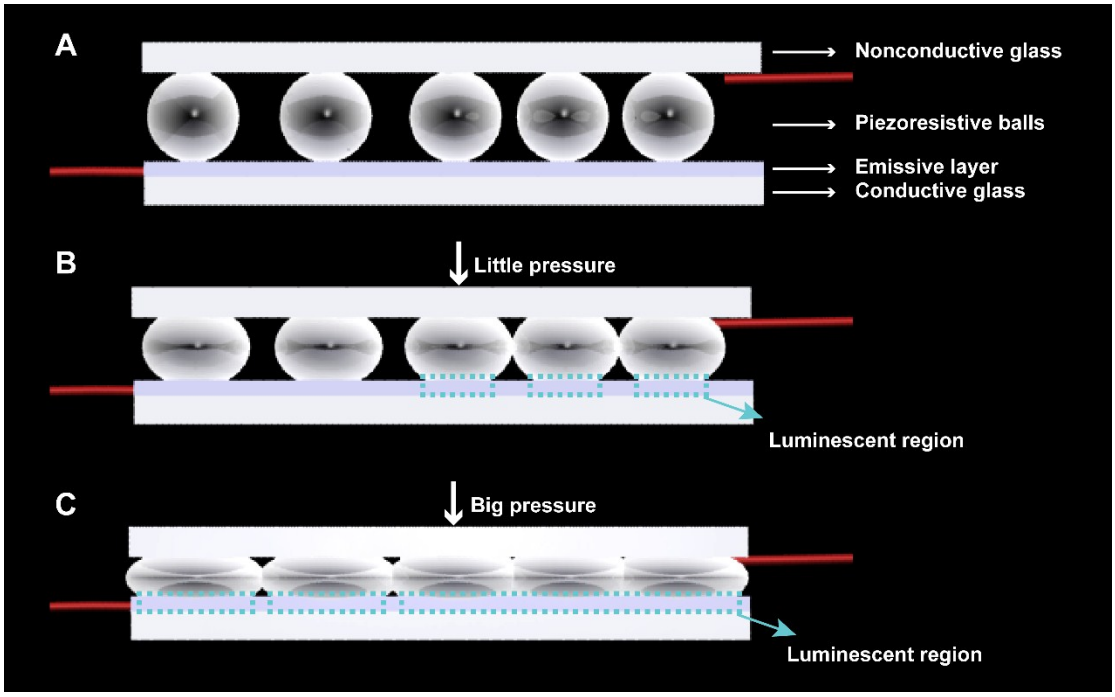

Fig. S9 Piezoresistive balls based optoelectronic devices in the (A) off, and on working states with (B) little pressure and (C) big pressure. The spaces of columns are different.

As shown in Fig. S9A, piezoresistive balls based optoelectronic device is in the off state, and the spaces of columns are different. The piezoresistive ball is squeezed and connects with electrode by providing little pressure (Fig. S9B). In addition, three columns of piezoresistive balls with small spaces are connected in turn and form conductive paths. When applying high frequency alternating voltage and providing little pressure, the optoelectronic devices emit a small area of blue luminescent light, because the luminescent region only appeared when the emissive layer is sandwiched between piezoresistive ball and conductive glass. However, when big pressure is provided, piezoresistive balls are largely squeezed and all columns of piezoresistive balls are connected in turn and form conductive paths (Fig. S9C). Thus, when applying high frequency alternating voltage and providing big pressure, the optoelectronic devices emit a large area of blue luminescent light.

References

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