Supporting Information

Ultrastable Perovskite–Polymer Exciplex through Self Energy-level Adaption for Underwater Light-emitting Devices

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Experimental methods

Fabrication of perovskite- emitting polymer blend in A-DCP matrix

The precursor of MAPbBr3 was prepared by dissolving 0.6 mmol MABr and 0.6 mmol PbBr₂ into 1 ml N,N-Dimethylformamide (DMF) and the resultant solution was stirred at room temperature for overnight. The poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) was dissolved in chloroform (CF) at a concentration of 20 mg/ml, the solution was stirred at room temperature for overnight. MABr and PbBr₂ was purchased from Xi'an Polymer Light limited. F8BT was purchased from 1-Materials Inc. and all the solvent was purchased from Sigma-Aldrich.

50 µl precursor of MAPbBr₃ dissolved in DMF is dropped into 500-µl acrylate monomer, 2-propenoic acid [octahydro-4,7-methano-1H-indene-2,5-diyl)bis(methylene) ester (A-DCP) with benzoin dimethyl ether (DMPA) of 0.5 wt.% with respect to the monomer for UV-light sensitization followed by vigorous stirring at room temperature; during the stirring, precipitate of MAPbBr₃ appear. After the formation of the MAPbBr₃ micro cubes, a CF solution of F8BT is directly injected into the suspension of MAPbBr₃ precipitate under continuous stirring. Finally, the resultant liquid is heated at 80 °C for 20 minutes to remove any unwanted solvent. All the process is carried out in a nitrogen-filled glovebox to avoid the influence of oxygen and moisture.

PL and absorption characterization

The steady state PL spectra was collected by an Edinburgh Instrument FLS920 Spectrometer with a Xenon lamp as excitation light source.

Time-resolved fluorescence was measured by a time-correlated single photon counting (TCSPC) module in the FLS920 Spectrometer. A 405 nm laser with the tuneable reputation rate was used as the excitation beam and a 455 nm high-pass filter was placed in front of the signal detector to block any scattered excitation light.

The steady absorption measurements were conducted using a Xe lamp and a USB4000 spectrometer (Ocean Optics).

For all the above-mentioned PL and absorption measurements, a homemade sample cabinet connected with a liquid helium compressor and a Cryogenic Temperature Controller (Lakeshore Ltd.) was used to control the sample temperature.

TA measurements

The TA measurements were carried out using a femtosecond pump-probe system, where a femtosecond laser (Legend Elite Series, Coherent Inc.) at 800 nm with a reputation rate of 1 kHz and pulse width of 150 fs was used as pump light after frequency-doubling by a β -barium borate crystal producing 400 nm pulses. A supercontinuum was generated by focusing a small portion of 800 nm femtosecond laser pulse to heavy water in a cuvette and used as the probe.

LED fabrication and characterization

To fabricate the UV-LED driven light emitting devices, the UV-LED chip was dipped into the blend indicated in Figure 1 and lifted out after 5 seconds then turn on the UV-LED to realize polymerization. The process was repeated three to ensure a sufficient thickness of the material at the surface of the UV-LED.

The UV-LED were driven by a Keithley 2400 at 3 V and various currents, the EL spectra were recorded using a USB4000 spectrometer (Ocean Optics).

The LED performance were characterized in ambient environment using a Keithley 2400 source meter and a Keithley 2000 multimeter connected to a calibrated Si photodiode (PDA100A2, Thorlabs). The luminous efficiency was calculated by assuming a Lambertian emission distribution from the devices.

UPS measurement

UPS experiments were performed using a Thermo Scientific Escalab 250Xi UPS/XPS Photoelectron Spectrometer with He I (21.22) eV photon lines. Binding energies were calibrated by measuring the Fermi step position and the Au 4f7/2 core level of a clean gold film.

SEM and XRD characterization

Morphology experiments were performed using a JEOL JSM 6510 emission scanning electron microscopy (SEM). The XRD examinations were carried out using a D8 Advance instrument.

3



Figure S1. XRD pattern of MAPbBr₃ single crystal.



Figure S2. Tauc analysis of F8BT and MAPbBr₃ to determine the energy band gap. For both materials, a direct band gap is determined and the bandgap are 2.44 (F8BT) and 2.22 (MAPbBr₃) eV respectively.



Figure S3. PL decay of (a) F8BT and (b) MAPbBr₃ in the photopolymer matrix at different temperatures.



Figure S4. PL spectra of (a) F8BT and (b) MAPbBr₃ in the photopolymer matrix at different

temperatures.



Figure S5. PL decay of F8BT- MAPbBr₃ blend in the photopolymer matrix measured at 550 nm.



Figure S6. The transient absorption spectra of (a) F8BT and (b) MAPbBr₃ in the photopolymer matrix.



Figure S7. Current density – luminance – voltage (J – L - V) characteristics of the UV-LED driven light



emitting devices.

Figure S8. The EL spectra of the LED devices before and after soaking in water for different times.

600

Wavelength (nm)

700

800

400

500



Figure S9. Emission spectra of the light emitting devices tested under continuous working conditions

at 3 V, 0.3 mA for different times.