Electronic Supplementary Information (ESI) available:

Experimental

All materials and chemicals were purchased commercially and used as received. $LiNbO_3$ (LN) was purchased from Deqingruiyang Optical Element Co., Ltd (Zhejiang, China) and was made by electric-field-pulling (Czochralski) method. PMMA, F8BT, and MEH-PPV were purchased from Sigma-Aldrich. PS was purchased from Polymer source, Inc. Other chemical reagents were purchased from Sinopharm Chemical Reagent Beijing Co. All the AFM images were recorded using a Veeco D3100 instrument and the SEM images were recorded with a JEOL 7401 microscope. Optical and Fluorescent images were recorded with a Nikon TE2000-U optical microscope.

Patterning of charge on LN: Uniformly polarized LN crystal (Z-cut) was contacted with a topographically patterned PDMS stamp (previously heated at 180 ℃ in order to adsorb and transfer heat) for 1s to accomplish the pyroelectricity and the procedure is similar as in literature [24].

Adsorption of nanoparticles: Charged LN was immersed into a 0.5% w/v suspension of polystyrene microspheres (60 nm) in ethanol for 60 seconds and quickly rinsed with water to remove the loosed attached part, and the results were recorded with SEM.

S*elf-assembly of polymer film on LN:* Different types of polymers were used : 1) polystyrene (PS) (Mw=27kg mol^{-1}) 2) poly(methyl methacrylate) (PMMA) (molecular weight Mw =350 kg mol^{-1}) 3) Polyvinyl Alcohol (PVA) (molecular weight Mw = 1750±50 g mol^{-1}) 4) 1%wt Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3] thiadiazol-4,8-diyl)] (F8BT) (molecular weight Mw = 5000-8000 g mol^{-1}) doped in PS 5) 1%wt Poly[2-methoxy-5-(2-ethylhexyloxy)- 1,4-phenylenevinylene] (molecular weight Mw =51000 g mol^{-1}) doped in PS. Films with thicknesses of 30-60 nm were spin-coated from 1wt% solution (PS in toluene, PMMA in chlorobenzene, PVA in water, F8BT mixed PS in xylene, and MEH-PPV mixed PS in toluene) onto LN. The surface of LN wafer was treated by air plasma (PDC-32G Plasma Cleaner, Harrick Plasma, NY) using medium level for 2 min before spin-coating PVA film.

The assembly in room temperature was taken in airtight chamber with saturated solvent vapor (F8BT mixed PS in xylene, MEH-PPV mixed PS in toluene) for 1-2h, and then dried in air for 1h.

The assembly above glass transition temperature of the polymer was taken at the temperature of 140 ℃, 170 ℃ and 90 ℃ for PS, PMMA and PVA respectively. After annealing, the samples were quenched to room temperature quickly. And the spin-coated progress was taken after cleaning the surface of discharged LN with water and ethanol.

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