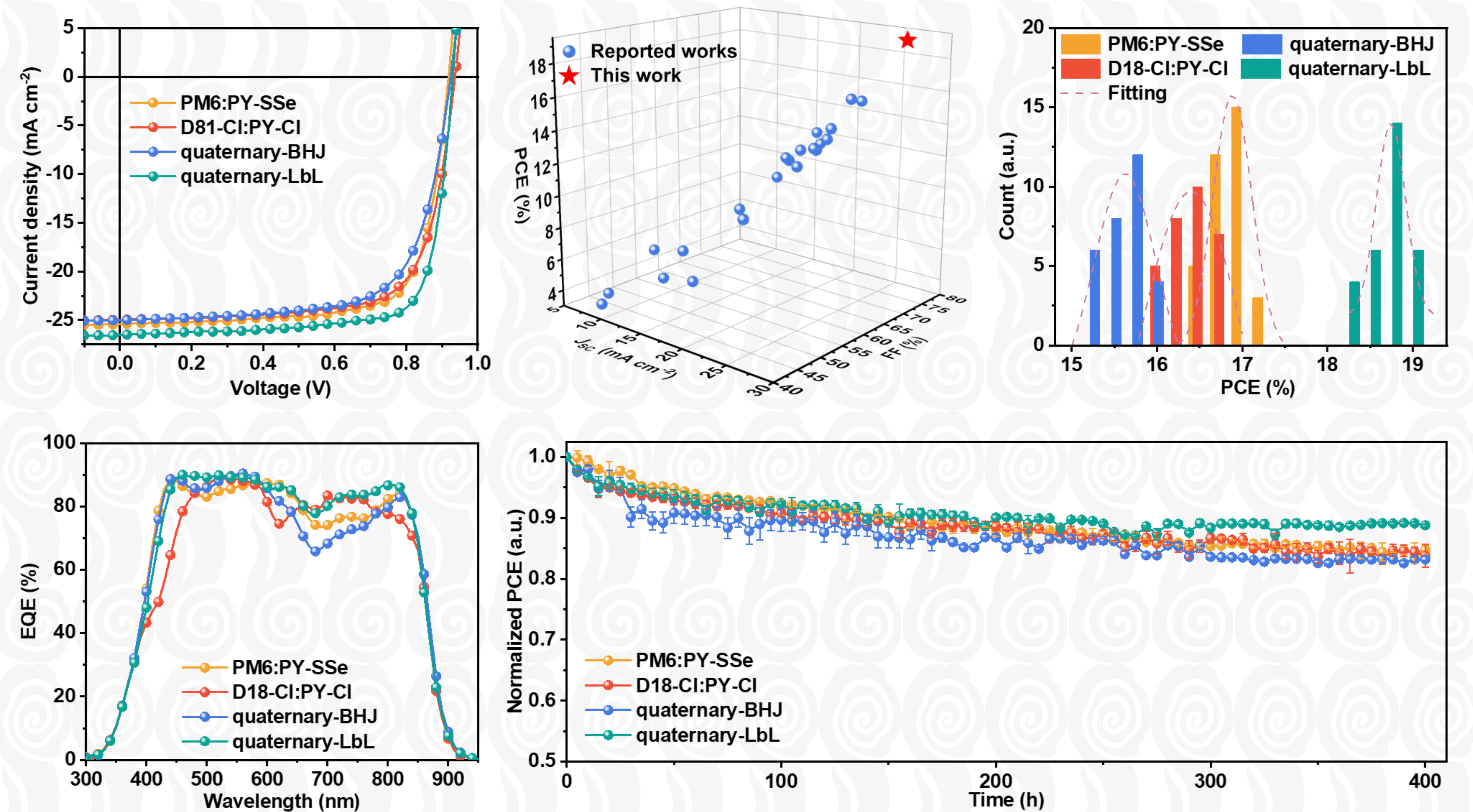
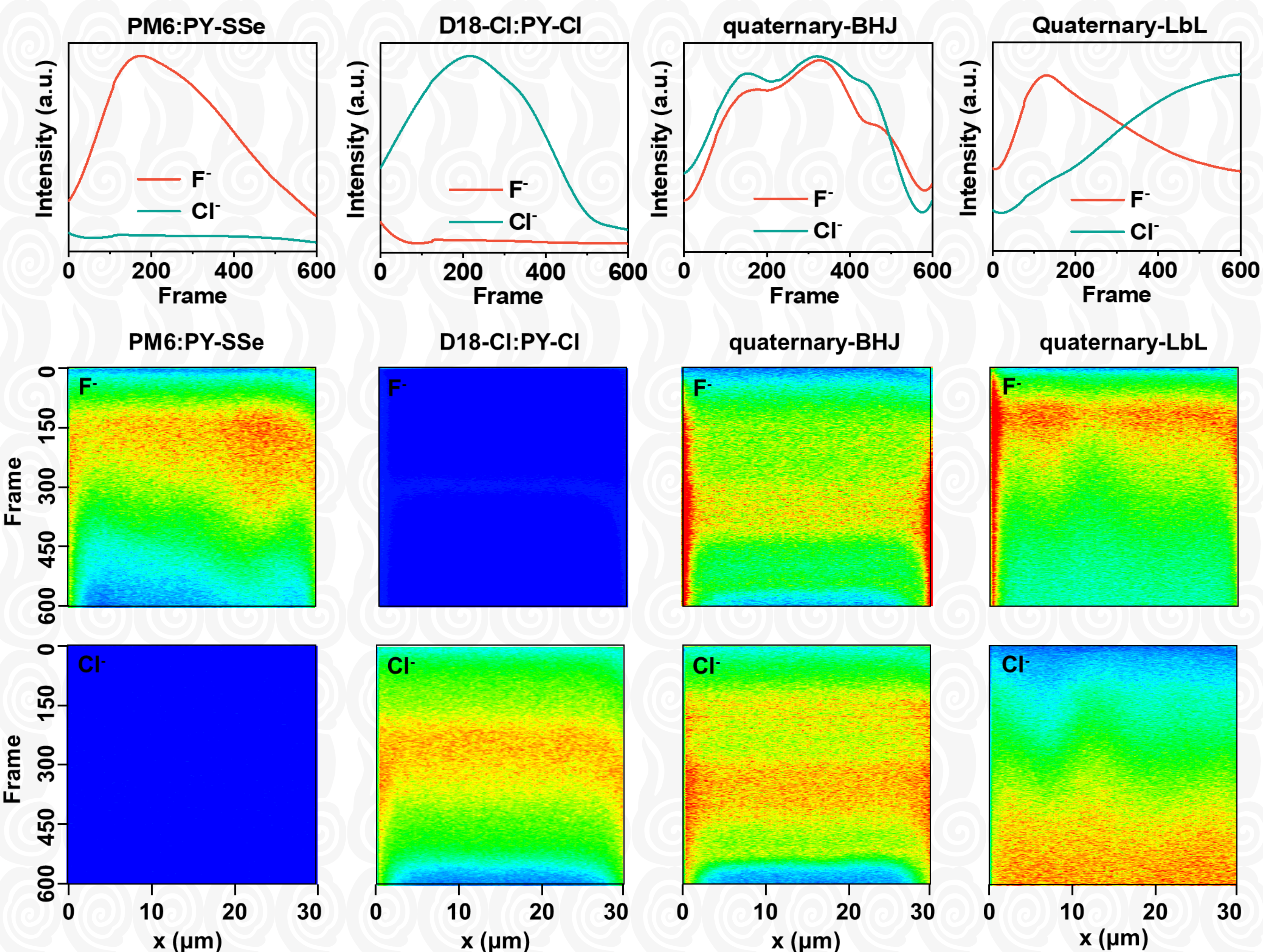


- Two highly efficient binary all-polymer donor-acceptor pairs are used to construct the quaternary system.
- Complementary absorption characteristics of the four materials finally result in a broadened and strong absorption spectra.



- Using blade-coating process, the PCE of PM6:PY-SSe system was 17.3%, with an open-circuit voltage (V_{OC}) of 0.919 V, a J_{SC} of 25.39 mA cm⁻² and a FF of 74.17%. D18-Cl:PY-Cl binary system exhibited a lower PCE of 16.85% (V_{OC} = 0.937 V, J_{SC} = 24.95 mA cm⁻², FF = 72.10%), for quaternary-LbL system, a PCE of 19% was achieved (V_{OC} = 0.930 V, J_{SC} = 26.52 mA cm⁻², FF = 77.03%).



- The signals of both F⁻ and Cl⁻ in the quaternary-BHJ blend film exhibited similar three stages of increasing, steadiness, and decreasing. These materials do not spontaneously form a vertical distribution under their interfacial interaction.
- The secondary F⁻ signal of the quaternary-LbL blend declined gradually while the Cl⁻ signal increased, this is directly caused by the sequential blade-deposition of PM6:PY-SSe and D18-Cl:PY-Cl BHJs.