Judicious incorporation of ambiopolar black phosphorene with tailored thickness to concurrently impart electron and hole extractions in perovskite solar cells is reported by Jinsong Huang, Zhiqun Lin, and co-workers in article number 2000999. This work underpins the potential implementation of black phosphorene as a dual-functional transport material for a diversity of optoelectronic devices, including photodetectors, sensors, and light-emitting diodes.