Supporting Information

High efficiency all-solution-processed LEDs based on dot-in-rod colloidal heterostructures with polar polymer injecting layers

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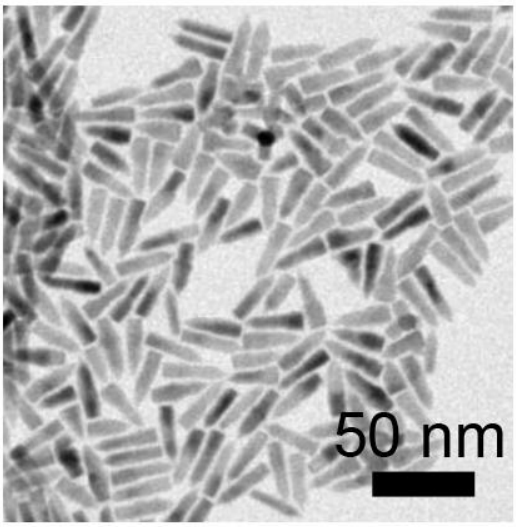
Supporting Fig.S1 Transmission electron micrograph of CdSe/CdS dot-in-rod QDs.



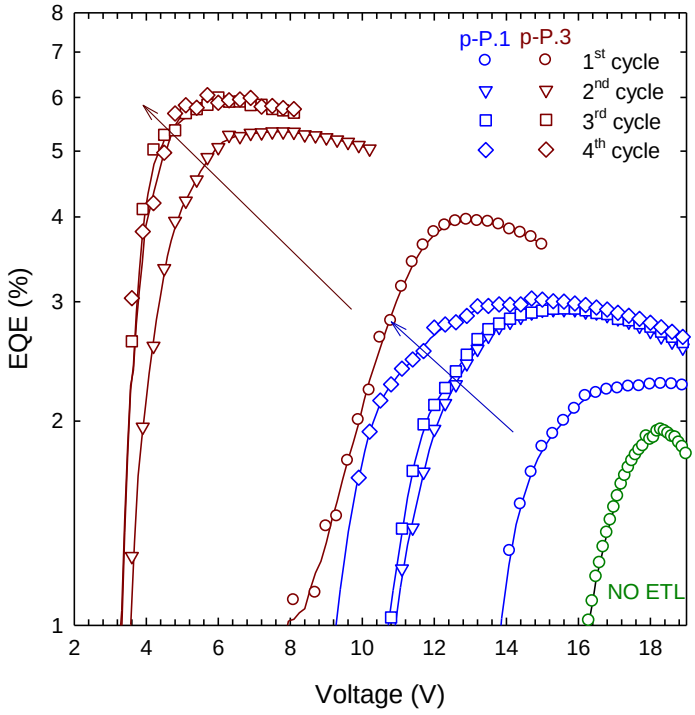
Supporting Fig.S1 Transmission electron micrograph of the CdSe/CdS dot-in-rods used in the QD-LEDs. The core diameter is 5.1 nm, the rod diameter is 6.8 nm and the particle length is 26.8 nm.

Supporting discussion

Conditioning of the polar polymer ETLs:

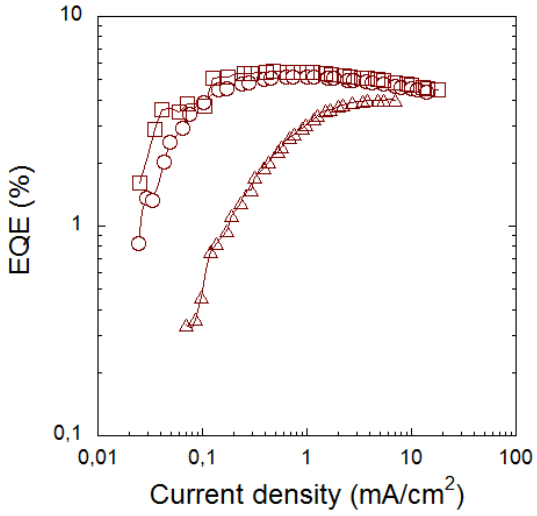
As mentioned in the main text, one key difference between non-conjugated dielectric interlayers and polar/electrolytic polymers, is that the latter introduce an electron barrier whose width evolves during device operation due to the alignment of the polar/ionic side chains with the electric field and accumulation of the cationic functionalities at the ETL/metal interface. This peculiar behavior is clearly observable looking at the electroluminescence response of the same device during successive driving cycles (Supporting Fig.S2). In the first voltage sweep, when the polar moieties are randomly oriented and the cations uniformly distributed in the film, we systematically observe higher V_{ON} together with slower saturation of the EQE with respect to the successive cycles, where V_{ON} progressively decreases and the EQE reaches faster higher absolute values. Devices incorporating any of the three polar polymer ETL show saturation of the EQE and V_{ON} in approximately 4 cycles, after which the behavior is stable for many consecutive sweeps, as typically observed in OLEDs and LECs.[29-31, 34] This indicates that the first driving cycles trigger the formation of polarized interfaces which are then maintained over time, stabilizing the device in its conditioned state with highly reproducible electroluminescence response. Importantly, in order for the conditioning to be successful, it is critical that the first sweeps are driven to sufficiently high voltages, which suggests that in our devices, similarly to OLEDs, the reorganization of the side-chains has to overcome a potential activation barrier[29-31]. Finally, the effect is more pronounced for p-P.**3** with respect to the non-electrolytic polar analogues, in agreement to the additional effect of the creation of a charged region at the ETL/cathode boundary[31, 34].

Supporting Fig.S2 Polarization of the polar polymer ETL during pre-conditioning driving cycles.



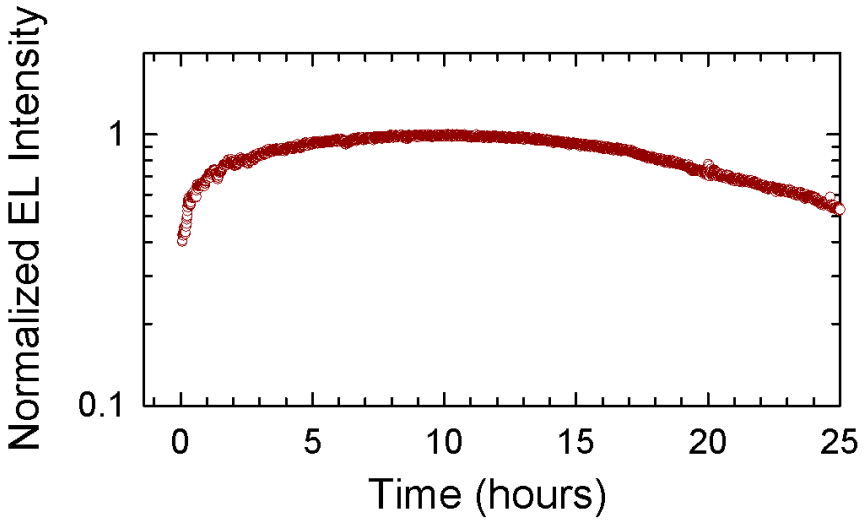
Supporting Fig.S2 External quantum efficiency (EQE,%) as a function of the driving bias (V) during four successive operation cycles of QD-LEDs (device structure ITO/PEDOT:PSS/PVK/DiRs/polar-polymer ETL/Ba/Al) incorporating polar/electrolytic polymer ETL (p-P.1, blue lines and symbols; p-P.3, dark red lines and symbols) in comparison to a control device with no ETL (green lines and symbols). For the QD-LEDs with ETL, the EQE curves shifts progressively in the first three cycles to lower voltage, according to the formation of polarized interfaces.

Supporting Fig.S3 Stability of DiR LEDs with electrolytic ETL



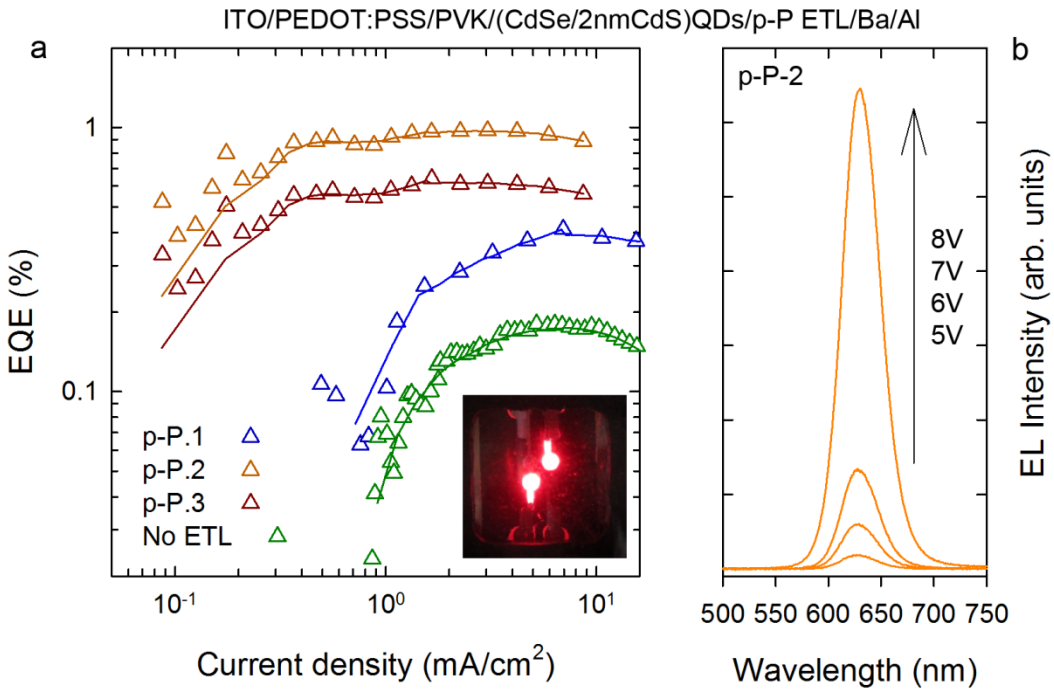
Supporting Fig.S3 EQE for a DiR-LED incorporating p-P.3 measured before conditioning (triangles), after four conditioning cycles (circles) and after 72 hours (squares) from conditioning, showing perfect retention of the EL performances.

Supporting Fig.S4 Stability of DiR LEDs with electrolytic ETL



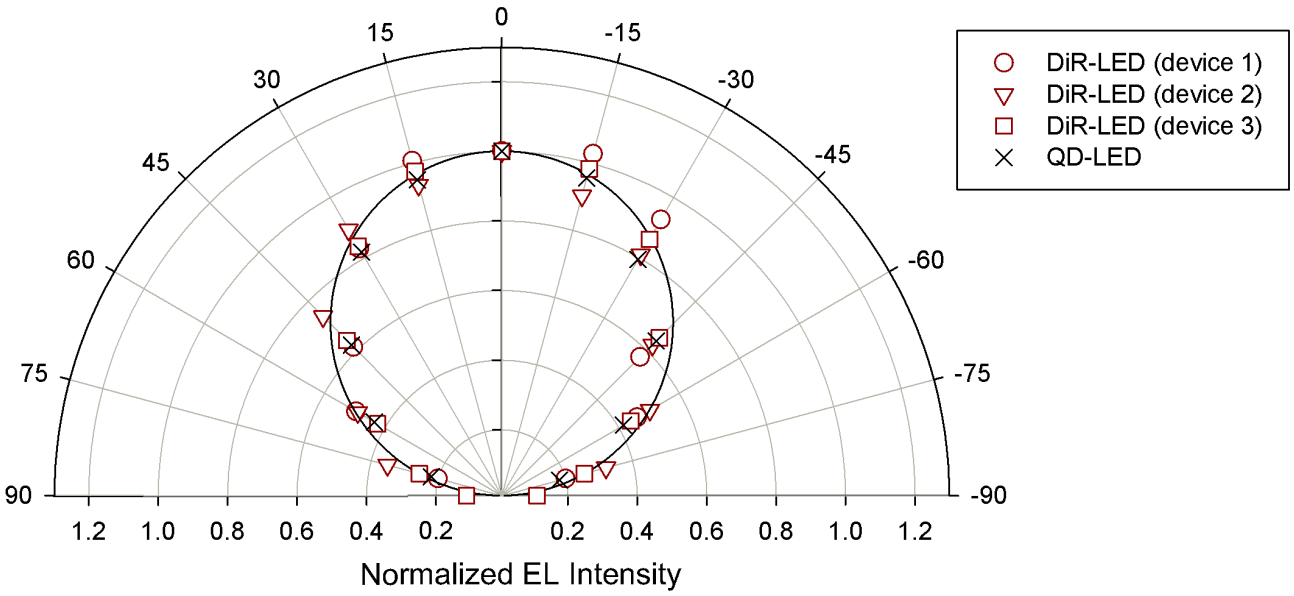
Supporting Fig.S4 Normalized EL intensity for a DiR-LED incorporating p-P.3 measured under constant operation for 25 hours (driving current of 10 mA/cm2 corresponding to driving voltage of 8-9 V).

Supporting Fig.S5 Electroluminescence performance of solution processed QD-LEDs incorporating polar polymer ETLs and spherical core/shell QDs.



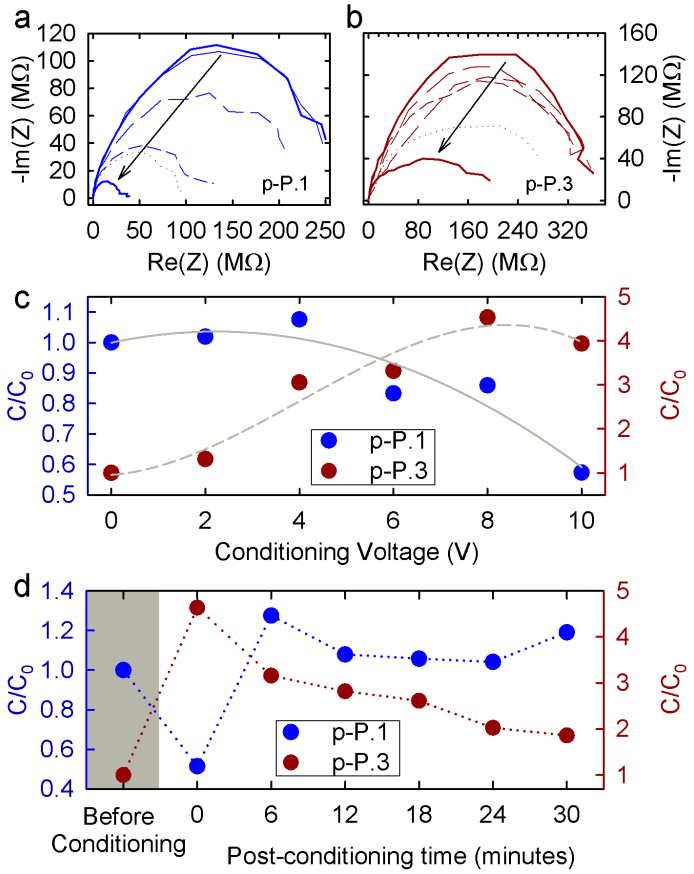
Supporting Fig.S5 (a) External quantum efficiency (EQE, %) as a function of the current-density-voltage for fully solution-processed QD-LEDs embedding CdSe/CdS core/shell QDs (core radius 1.2 nm, shell thickness 2 nm) and different polar/electrolytic polymeric ETLs (device structure ITO/PEDOT:PSS/PVK/QDs/polar-polymer ETL/Ba/Al). (b) Electroluminescence spectra of a device embedding p-P.2 at increasing driving bias. The same colour scheme applies to the whole figure.

Supporting Fig.S6 Angular emission profile of solution processed QD-LEDs incorporating spherical core/shell QDs and anisotropic CdSe/CdS DiRs.



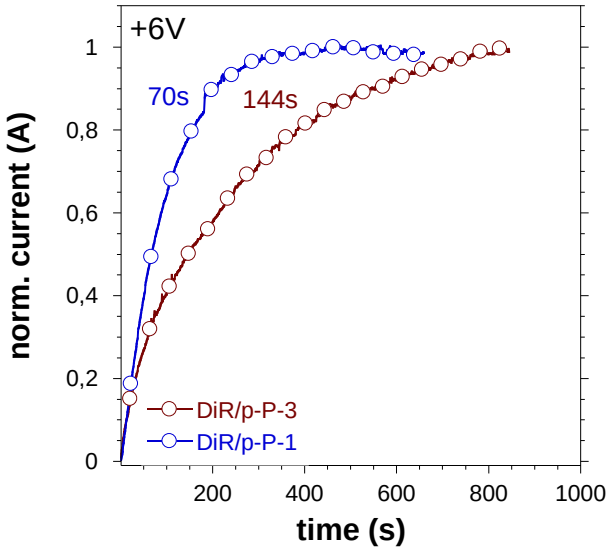
Supporting Fig.S6 Angular emission profile of solution processed QD-LEDs incorporating spherical core/shell QDs (black crosses) and anisotropic CdSe/CdS DiRs (symbols indicate different devices). All LEDs have the same p-P.3 ETL. The black line indicate the expected angular intensity distribution for a perfectly Lambertian emitter.

Supporting Fig.S7 Electric characterization of DiR-LEDs embedding polar or ionic ETLs



Supporting Fig.S7 Nyquist plots of impedance at various stages of the conditioning process from V=0 V to V=10 V (2V steps, indicated by black arrows) for LEDs incorporating (a) p-P.1 and (b) p-P.3. The curves corresponding to V=0V (unconditioned device) and V=10V are highlighted by bold curves. For each curve, except for unconditioned devices, constant voltage has been applied for 30 seconds before measuring. No constant bias is applied during the frequency scan. The analysis of each curve, formed by Z'-Z" values at different frequency of the probing oscillating electric field of ±0.1 V, shows one RC contribution. (c) Normalised device capacitance at the different stages of the conditioning process extracted from the data in (a) and (b). The LED with polar ETL shows progressive drop of capacitance upon conditioning, whilst the device with ionic ETL undergoes progressive increase of capacitance due to ion accumulation at the DiR-ETL interface. (d) Evolution of the device capacitance after conditioning at 10V for 5 minutes for LEDs embedding p-P.1 (blue dots) and p-P.3 (dark red dots). The same colour scheme applies throughout the figure.

Supporting Fig.S8 Electric characterization of DiR-LEDs embedding polar or ionic ETLs: time evolution of the device current at constant voltage bias



Supporting Fig.S8 Evolution of the (normalized) device current for unconditioned LEDs embedding p-P.1 (blue dots) and p-P.3 (dark red dots) under constant forward bias of 6V.