OLED from solution-processed crystalline poly(triazine imide)

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Experimental

Synthesis of PTI-LiBr: 1 g of precursor dicyandiamide (DCDA, Sigma Aldrich >99%) is ground with a vacuum dried eutectic salt mixture of LiBr and KBr (Sigma Aldrich /Acros Organics >99%) (15 g; 52:48 wt%, m.p. 348°C) in a glovebox. The reaction mixture is filled into a quartz ampule and sealed. The sealed quartz ampule is placed vertically into a furnace (Nabertherm, L 5/11/B180, 2.4 kW) at 400 °C for 4 h. Then the temperature is increased (10 K/min) to the final condensation temperature for the desired timeframe. The ampule is removed at room temperature, opened, and the salt block is dissolved in dest. Water in a 50 mL Falcon. The slurry is centrifuged and the supernatant is decanted. The pellet is re-dispersed in hot water on a shaker and centrifuged again. The supernatant is decanted and the process is repeated for two times with hot water and two times with methanol (>99% for synthesis). The resulting pellet is redispersed in methanol and the methanol is evaporated. The resulting powder is dried under vacuum at 200 °C for 24 h. The furnace geometry and temperature homogeneity play a role for the synthesis of organic materials at temperatures close to carbonization. For repeatable experiments the ampule should be placed at the same spot in the furnace.

PTI-IF was obtained following the procedure proposed by Suter et al. (https://doi.org/10.1039/C8SC05232H) using PTI-LiBr synthesized at 550 °C for 48 h.

First-principle calculations: First-principles calculations are performed on model monolayer structures featuring various protonation conditions – see Figure S7. The unit cell of the PTI monolayer is formed by 18 atoms which comprise the two triazine rings and three imide bridges atoms and the system is assumed to be periodic only in the planar directions. 10 Å of vacuum are included in the directions perpendicular to the layer to avoid unphysical interactions between the replica. Protonation is realized by placing one dissociated HCl molecule per unit cell in proximity to the protonation site (nitrogen at one triazine ring or nitrogen at one imide-bridge, see Figure S7a) and then relaxing the system. The explicit inclusion of the Cl counterion ensures charge neutrality and includes the electrostatic effect of the anion on the protonated system. The equilibrium position of the Cl⁻ ion, relative to the protonated backbone, is obtained with a further structural optimization of the whole system that places it at the pore centre as shown in Figure S7b-c.

Ground state calculations are performed from spin-restricted DFT [Hohenberg P and Kohn W Phys. Rev. 136 B864 (1964) and Kohn W and Sham L J Phys. Rev. 140 A1133 (1965)] as implemented in the pseudopotential, plane-wave code Quantum Espresso (QE). A uniform 6x6x1 k-mesh is adopted to sample the Brillouin zone, the PBE functional [REF Perdew J P, Burke K and Ernzerhof M Phys. Rev. Lett. 77 3865 (1996)] is used to approximate the exchange-correlation potential, optimized norm conserving pseudopotentials are employed with 50 Ry (200 Ry) plane-wave cut-off to represent the wavefunctions (charge density). The pairwise Tkatchenko-Scheffler scheme [A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009)] is adopted to include dispersion interactions. The structures are optimized without imposing any symmetry constraint until residual interatomic forces are smaller than 10⁻⁵ Ry/Bohr. Optical absorption spectra reported are computed from time-dependent DFT [Runge and Gross Physical Review Letters. 52 (12): 997–1000 (1984)] in the linear-response approach. For these calculations the turbo-TDDFT routine of QE is used, implementing the Liouville–Lanczos algorithm. A Lorentzian of 130 meV is applied to each peak.

Preparation of PTI-LiBr dispersions: Sonication of Flakes was conducted with a BANDELIN HD 2200-U (200 W, HF 20 kHz) sonotrode setup with a MS72 sonotrode with the amplitude set to 30 µm with 5 mL dist. water. The 50 µL of PTI-LiBr and 5 mL of PTI-LiBr were added into a Falcon tube. The Falcon tube is placed in an ice bath and the so...
**SUPPORTING INFORMATION**

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\sigma = \frac{1}{\rho} = \frac{L}{U \cdot T \cdot A} = \frac{L}{U \cdot T \cdot w \cdot t}
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\( \rho \) = electrical resistivity
\( \sigma \) = electrical conductivity
\( U \) = bias
\( I \) = current
\( A \) = surface area
\( w \) = channel width
\( t \) = film thickness
\( L \) = channel length

**Film thickness measurements:** For extraction of conductivity film thickness values have been obtained with an Olympus LEXT laser scanning microscope.

**Fourier transform infrared (FT-IR):** Spectra were recorded from solid on a Thermo Scientific Nicolet iS5 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) in the wavenumber range of 4000-600 cm\(^{-1}\) with resolution of 4 cm\(^{-1}\).

**Raman:** UV Raman spectra were recorded with a Horiba T64000 spectrometer in single-grating mode. The excitation source was provided by a diode-pumped solid-state laser from CryLas at a wavelength of 266 nm and power of 4 mW. The light was focused on the sample with a Thorlabs LMU-40x-UVB objective (backscattering geometry). A notch filter with cut-off at 220 cm\(^{-1}\) was used to filter out the elastically scattered light. The acquired Raman spectra were calibrated by comparison with the spectrum of a Ga\(_2\)O\(_3\) crystal by using a quadratic calibration curve. This procedure allows for reduction of the experimental error at approximately 5 cm\(^{-1}\), which is below the spectral resolution of 8 cm\(^{-1}\).

**Powder X-ray:** Structural analysis of the prepared PTI-MX was performed with a Bruker D2 Phaser X-Ray powder diffractometer (XRD) in Bragg-Brentano geometry. X-rays were generated by a Cu K\(_{α1, α2}\) source at 30 kV operating voltage and collected with a LynxEye detector.

**Photoluminescence, Photoluminescence excitation, quantum yield, Lifetime:** Edinburgh Instruments FLS 980 spectrometer. Photoluminescence, photoluminescence excitation and quantum yield were measured using a Xe lamp. The quantum yield was determined in a direct excitation set up with an integrating sphere. Films were drop-casted from ethanol dispersions on quartz substrates PGO 10x10x0.5 mm. Further, it is important to note that the presented samples were prepared and characterised on the same day. Diffusion of protons in PTI-LiBr has not been studied yet. It is possible that crystals of PTI-LiBr are not fully protonated because the system has had not enough time to equilibrate. This might explain why the luminescence of the basic Li-defect is still present in acidic solutions. Lifetime measurements were conducted with an Edinburgh Instruments 375 nm pulsed laser set to a 50 ns pulse period. Evaluation was conducted with the instrument software choosing a two exponential decay function.

**UV-Vis:** UV-Vis-measurements were performed in ambient conditions with a PerkinElmer Lambda 950 spectrometer in standard transmission operation, 1 nm step size. Films were measured on 10x10x0.5 mm quartz substrates. Dispersions were measured in a quartz cuvette with 1 cm optical path.

**XPS:** JOEL JPS-9030 Photoelectron Spectrometer with an Al Ka (1486 eV) excitation source and a monochromator. Quantitative comparison of nitrogen and carbon in single spectra were performed by signal integration after background subtraction of a Shirley function. The samples were prepared by drop-casting PTI dispersions (MeOH) on ITO coated glass substrates to minimize charging and to avoid background carbon signals from e.g. carbon tape as substrate.

**ssNMR:** Cross polarization magic-angle spinning (CP-MAS) solid-state NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer operating at 100.6 MHz (\(^{13}\)C).

**SEM:** SEM images have been recorded with a GeminiSEM 500 electron microscope (Carl Zeiss GmbH, Germany).

**OLED preparation:** ITO-coated glass substrates (sheet resistance = 20 Ω per square) were cleaned by sequential sonication (10 minutes) in (i) acetone and (ii) isopropanol followed by drying via a nitrogen gun. The substrates were then treated via O\(_2\) plasma (partial pressure 1.2 x 10\(^{-1}\) mbar) for 15 minutes at 10.2 W. 50 nm PEDOT:PSS (Osilla) films were spin coated as hole injection layer and heated to 220 °C for 10 min. PTI-LiBr was drop casted from solution. 5 nm Calcium and 200 nm Aluminium were evaporated in a PVD chamber at 10\(^{-5}\) mbar. Finally the OLEDs were encapsulated with UV-curable resin (Osilla) and a glass slide. Current density–
voltage–luminance characterization was performed with a Keithley 2612B source meter and a Konica Minolta LS-160 luminance meter in a purpose-built setup. Electroluminescence spectra were taken with a CS2000 spectrometer (Ocean Optics) using OceanView software.
**SUPPORTING INFORMATION**

**Figure S1.** Three vials with the product of the condensation reaction at 550 °C, 48 h, 600 °C, 12 h and 600 °C, 72 h are depicted. Underneath are the corresponding films on quartz substrates drop casted from dispersion for the 550 °C 48 h product, 600 °C 12 h and 600 °C 72 h product. The brown color is a result of on setting carbonization and leads to self-absorption and deteriorates charge transport through the polycrystalline material.

**Figure S2.** Solid state NMR (ssNMR) of PTI-LiBr obtained from conditions reported in literature 600 °C 12 h and at lower temperature 550 °C, 48 h. The spectrum obtained from the product synthesized at lower temperature has sharper bands. The three observed bands correspond to three carbon environments present in PTI-LiBr as well as PTI-LiCl at 167.0 ppm 162.0 ppm and 158.0 ppm.
**Figure S3.** Morphology studies of PTI-LiBr product. a) The anticipated hexagonal platelets of PTI-LiBr (5 kV acceleration voltage). b) PTI-LiBr product after 30 min sonication (20 kV acceleration voltage). SEM pictures after sonication show typically a film of debris covering all structures.

**Figure S4.** a) FT-IR of PTI-LiBr product from 525 °C for 48 h b) PXRD of PTI-LiBr product from 525 °C for 48 h compared to 550 °C for 48 h. Additional contributions in the NH region and additional PXRD peaks indicate incomplete condensation.
De-intercalation of PTI-LiBr results in more defined IR and Raman bands. PTI-LiBr has an unexpected strong Raman signal at $1088 \text{ cm}^{-1}$. This could be due to formation of small amounts of lithium carbonate in a surface reaction. The lithium defect can undergo hydrolysis in presence of atmospheric water. The reaction of LiOH with atmospheric CO$_2$ results in lithium carbonate. The PXRD of PTI-IF shows the loss of the graphitic order after removing the structure directing salt ions.
Figure S6. HCl (0.1 M) titration of 26 mg PTI-LiBr (550 °C, 48 h) dispersion. The second equivalence point at pH 5 corresponds to the pH region where also changes in the optical spectra take place (emergence of 330 nm, 420 nm photoluminescence and 260 nm absorption band).

Figure S7. PTI single monolayer relaxed structures in-vacuo, relative to PTI-IF (a), the triazine-protonated (b) and the imide-bridge protonated (c) backbones. In the protonated structures we have also reported the formation energies per unit-cell volume evaluated as the difference between the total energy of the protonated system and the sum of the energies of the separated pristine monolayer and HCl subsystems.
Figure S8. Electronic bandstructures of pristine PTI-IF (gray lines) and triazine / imide-bridge protonated-PTI (blue dashed lines).
**Figure S9.** a) Comparison of photoconductor employing PTI-LiBr from 600 °C and 550 °C. Charge transport and photocurrent are absent in the 600 °C material due to the observed partial carbonization (black line). In the device employing PTI-LiBr from 550 °C current is able to cross the channel of the interdigitated substrate and photocurrent is observed when excited with a 375 nm LED focused on the device with a lens. b) Irradiance dependent IV sweep of photoconductor device. Increased irradiance with a 375 nm LED results in increased current flow. The low current is result of the polycrystalline material property (grain boundaries) and likely energetic disorder at partially intercalation free layers. b) IV sweeps of an interdigitated device employing 550 °C, 48 h product with different sweep speed. The observed hysteresis is due to migration of Li⁺ and Br⁻ ions.