Supporting Information

Hexacyano-[3]-radialene anion-radical salts: a promising family of

highly soluble p-dopants

Y. Karpov, N. Kiriy, M. Al-Hussein, M. Hambsch, Tetyana Beryozkina, Vasiliy Bakulev, S.

Mannsfeld, B. Voit, and A. Kiriy*

Materials

Chemicals and solvents were purchased from Aldrich and used as received if another not stated.

P3HT was purchased from Sigma Aldrich, extracted on Soxhlet apparatus with aceton, hexane and DCM. DCM fraction (Mn 68 kg/mol, PDI 2.1 according to our GPC, 40 $^{\circ}$ C in CHCl₃) was used for film preparation.

Instrumentation.

1H NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for 1H using a 5 mm 1H/13C/19F/31P gradient probe. The samples were measured in C2D2Cl4 as solvent at 120°C. The spectra were referenced on the residual solvent peak $(\delta(1H) = 5.98 \text{ ppm})$.

Mass spectra were recorded on Maldi TOF Autoflex speed LRF, Bruker Daltonik.

Cyclic voltammetry. Cyclic voltammetry (CV) measurements were performed under nitrogen atmosphere in a freshly prepared anhydrous and deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate in acetonitrile (0.1 M) containing small amounts of the analytes. The three-electrode setup consisted of a platinum disc working electrode and platinum wires as counter electrode and pseudo-reference electrode. The voltammograms were recorded at a scan rate of 50 mV·s⁻¹ and referenced to the half-wave potential of the added internal standard ferrocene, adjusted here to 0.00 V. The transfer to the Fermi energy was based on Trasatti's report³⁰ about -4.44 eV being equivalent to 0.0 V vs. NHE (normal hydrogen electrode) which results in E(Fc/Fc+) = -5.09 eV.

UV-Vis-NIR absorption spectroscopy. Cary 5000 UV-Vis-NIR (Agilent Technologies) at a scan rate of 20 nm \cdot s⁻¹ was used to record UV-Vis-NIR absorption spectra of solutions in quartz cuvette (pathlength 1 mm) or thin polymer films prepared by drop casting on glass.

The atomic force microscope (AFM). The microscope (Bruker, Dimension Icon) was operated in tapping mode using silicon-SPM-sensors (BudgetSensors, Bulgaria) with spring constant of ca. 40 N/m and resonance frequency of ca 300 kHz. Thickness of the polymer layers was measured using a scratch test technique.

Thermogravimetric analyses were carried out on a TA Instruments Q500 with a heating rate of 10 K/min under a flow of nitrogen, using Pt crucibles and 10 mg of sample for each analysis.

X-ray Scattering. Grazing incidence wide-angle X-ray measurements (GIWAXS) of thick films (about 1 µm) were performed using a Bruker D8 Discover diffractometer operating at 1.6 kW. The diffractometer is equipped with a Cu Twist tube, Ni filter ($\lambda = 1.5418$ Å), Goebel mirror, and 0.3 mm PinHole collimator for the incident beam. The sample was mounted on an Eulerian Cradle with automatic controlled X–Y–Z stage. The GIWAXS patterns were recorded with a VÅNTEC-500 area detector using a sample-to-detector distance of 105 mm and an incident angle of 0.5°. High resolution specular data were obtained using a 2-circle diffractometer (XRD 3003 T-T, Seifert-FPM) and a point detector. By employing a parabolic multilayer mirror, a highly parallel beam of a monochromatic Cu-K α radiation ($\lambda = 1.5418$ Å) was obtained.

The GIWAXS experiments of thin doped films (200 nm) were performed at the ID-10 beamline of the European Synchrotron Radiation Facility (Grenoble, France). The 2D diffraction patterns were collected with a Pilatus 300k detector ($172x172 \mu m^2$ pixel size). The wavelength used was 1.24 Å. The measurements were performed on thin films deposited on Si substrates at an incidence angle of 0.2 deg. The modulus of the scattering vector **q** was calibrated using several diffraction order of silver behenate. In-situ heating ramps were performed with a Linkam heating stage. The data correction and reduction was performed with home-made routines written in Igor Pro software.

Synthesis of disodium 2,2',2''-(cyclopropane-1,2,3-triylidene)trimalononitrile dianione (CN6-CP²⁻/2Na⁺). Solution of malonodinitrile 5.57 g (84.3 mmol) in 10 ml dry dimethoxyethane was slowly added to suspension of 4 g (168 mmol) sodium hydride in 100 ml dry dimethoxyethane under an argon atmosphere, at temperature 0°C. The mixture was stirred for 1h and then tetrachlorocyclopropene (1) 5.24 g (29.5 mmol) was added drop by drop to the reaction vessel. After 2 h stirring fine solid was filtrated, washed with water and diethyl ether. Yellow powder was dried overnight in vacuum oven at 60 °C. Yield 82%. ¹³C NMR, δ : 124.62 (C-ring), 121.07 (CN), 24.87 (methylene).

Synthesis of potassium 2,2',2''-(cyclopropane-1,2,3-triylidene)trimalononitrile anioneradical (CN6-CP^{•-}/K⁺). 0.74 g (2.74 mmol) of potassium persulfate was dissolved in 40 ml of water in a beaker. 0.5 g (1.82 mmol) of (CN6-CP²⁻/2Na⁺) was added by several small portions. Solution color immediately changed into deep blue-purple. After 2h stirring solid was filtrated through fine-porous glass filter and deep-purple crystals were obtained. Solid was washed with water and dried overnight in vacuum oven at 60 °C. Yield 91%. Compound gave no signal in NMR experiments due to the radical nature. MALDI TOF, m/z: 228 [M⁻], 266, 267 [M+K⁺], 202 [M⁻-CN].

Synthesis of tetrabutylammonium 2,2',2''-(cyclopropane-1,2,3-triylidene)trimalononitrile anione-radical (CN6-CP[•]/TBA⁺). 0.30 g (1.09 mmol) of potassium persulfate was dissolved in 25 ml of water in a beaker. 0.2 g (0.73 mmol) of (CN6-CP²⁻/2Na⁺) was added by several small portions. Solution color immediately changed into deep blue-purple. After 10 min stirring 0.213 g (0.77 mmol) of tetrabutylammonium chloride was added and after 30 min stirring black solid was filtrated through fine-porous glass filter. Deep-purple solid was washed with water and dried overnight in vacuum oven at 60 °C. Yield 52%. ¹³C NMR, δ : 57.68, 23.08, 19.09, 13.29. 1H NMR, δ : 3.16 m (2H), 1.58 m (2H), 1.34 m (2H), 0.96 m (3H). MALDI TOF, *m/z*: 228 [M⁻], 202 [M⁻-CN], 242.43 [N⁺(CH₂)₃CH₃].



Figure S1. NMR ¹H CP²-NBu₄: a general overview and selected area.



Figure S2. NMR ¹³C CP²⁻NBu₄.



Figure S3. NMR ¹³C of CP²-Na⁺



Figure S4. I-V characteristics for doped blend films P3HT/CPTBA of the thickness of 200 μ m for corresponding molar doping ratios (MDR).



Figure S5. (a) Cyclic voltammograms of CN6-CP^{•–}/TBA⁺ (a) and P3HT (b) in 0.1 M *n*-Bu₄NPF₆ acetonitrile solution at 50 mV·s⁻¹ scan rate referenced to ferrocene (E(Fc/Fc⁺)_{1/2} was adjusted to 0.0 V). Multiple oxidation peaks are most likely due to a polycrystalline nature of P3HT films and the formation of polarons due to oxidation of the polymer located in more crystalline and ordered domains correspond to peaks with smaller voltages, whereas peaks with larger potentials are responsible for oxidation of amorphous domains. In addition, the peak at largest voltage is responsible for the formation of bipolarons.





Figure S6a. Differential (blue line) and integral (green line) TGA traces of CN6-CP^{•-}/TBA⁺. Weight loss occurred before 180°C is presumably due to remaining solvents.



Figure S6b. Differential (blue line) and integral (green line) TGA traces of $CN6-CP^{\bullet-}/K^+$.



Figure 7. UV–vis spectra for P3HT:CN6-CP $^{\bullet-}$ /TBA⁺ *solutions* at different MDRs as well as of the neat components.

Sample preparation

Solution doping. Polymer solution was prepared in chloroform with concentration 1 g/l to achieve the desired molar doping ratio, MDR, MRD=[CN6-CP^{•-}/TBA⁺]/[P3HT] and filtered through nanoporous 0.2 μ m PTFE filter. Then corresponding amount of dopant solution was added and the mixture was filtered through 0.2 μ m PTFE filter again. Doped polymer solution was slowly drop-casted onto freshly cleaned thin glass slides and left overnight for slow evaporation covered by Petri dish. The mean thickness of the doped films was determined by AFM measurements of scratched films and, for a given film, the measurements were repeated 3 times in 3 different positions. The measurements reveal a good thickness on film edges. To get consistent results, the electrical measurements were performed only in areas with uniform thicknesses. The obtained thickness values were in the range of 1 μ m which is in a good agreement with expected thicknesses calculated from the known concentration of the components, volume of the solution and the film area, assuming that the films are uniform.

Characterization.

Electrical measurements. Electrical conductivity of the doped films was measured by a standard method by using commercially available Loresta-GP MCP-T610 device (Mitsubishi Chemical Analytech) with standard ESP 4-pin in a line probe (measuring range $10^{-3}-10^7 \Omega/sq$). The distance between the current electrodes is 15 mm and between the potential electrodes is 5 mm. At least 6 measurements of square resistivity (ρ s) were performed for each sample in different positions on the film surface. Conductivity σ was calculated as $\sigma = 1/\rho s x t$, where t is the film thickness in cm. To perform measurements of $\rho s > 10^7 \Omega/sq$ for the undoped polymer, Hiresta-UP MCP-HT450 device with URS standard probe was used.

Bottom-contact devices. Highly doped silicon wafers with 300 nm SiO₂ were used as substrates. For the electrodes 2 nm Cr and 50 nm Au were thermally evaporated through a shadow mask at a vacuum of ~ 10^{-7} mbar. The electrodes have a width of 4.5 mm and 11 mm and the distance between two electrodes is 200 µm. For the current-voltage (IV) measurement a manual probe station (Cascade Microtech GmbH) and a Keysight B1500A Semiconductor Device Parameter Analyzer were used. IV-sweeps for voltages of 0 – 10 V were performed for each substrate with the different molar doping ratios (3 sweeps). The linear current-voltage dependencies were extracted and the resistance of each sample was calculated due to the Ohm's law

$$R = \frac{V}{I}.$$

From the resistance the conductivity of the film was calculated based on Pouillet's law

$$\sigma = \frac{1}{\rho} = \frac{l}{RA} = \frac{l}{Rtw}$$

where ρ is the resistivity, *l* the distance between two electrodes, *t* is the thickness of the doped film, and *w* is the width of the electrodes. The exact distances between two electrodes were measured for every sample with optical microscopy.



Figure S8. Optical microscope images of (a) P3HT film, (b) $CN6-CP^{\bullet-}/TBA^{+}$ film and P3HT:CN6-CP^{•-}/TBA⁺ films with (c) MDR = 0.03, (d) MDR = 0.10, (e) MDR = 0.20, (f)

MDR = 0.33, (g) MDR = 1.0, (h) MDR = 1.0 annealed at 120 °C for 10 min. It is evident that for MDR 0 - 0.03 an essentially homogenous phase is exhibited by the blend films. However, for MDR > 0.03 two distinctive regions are observed indicative of phase separation.



Figure S9. AFM tapping mode topography images of P3HT (a) and P3HT: $CN6-CP^{\bullet-}/TBA^+$ blends at different MDRs: 0.01 (b); 0.1 (c); 0.2 (d); 0.33 (e); 1 (f).



Figure S10. (a) and (b) GIWAXS patterns of neat films of the P3HT polymer and CN6- $CP^{\bullet-}/TBA^+$ dopant, respectively. (c) and (d) High resolution specular X-ray curves of neat films of the P3HT polymer and CN6- $CP^{\bullet-}/TBA^+$ dopant, respectively.