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Dipole Switchable Poly(*para*-phenyleneethynylene)s: Ferroelectric Conjugated Polymers

Soh Kushida,[a] Emanuel Smarsly,[a] Maximilian Bojanowski,[a] Irene Wacker,[b] Rasmus R. Schröder,[b] Osamu Oki,[c] Yohei Yamamoto,[c] Christian Melzer,[b] and Uwe H. F. Bunz*[a],[b]

Dedication ((optional))

Abstract: Dipolar 2,3-difluorobenzene-units are introduced into the backbone of a poly(*para*-phenyleneethynylene) (PPE) to generate a ferroelectric conjugated polymer. The structural features of the partially fluorinated PPE allow for the generation of a remanent polarization in the solid state: The difluorinated benzene rings behave as molecular rotors at high temperature, while at room temperature, stacking of such rings clamps down the ring orientation. The molecular dipoles can still be oriented by moderate external electrical fields at room temperature, and this PPE is then a ferroelectric. The concept should be transferable to other poly(aryleneethynylene)s and novel conjugated ferroelectric conjugated polymers will be accessible using this concept.

Ferroelectric materials and molecules change their polarization upon application of an external electric field. [1,2] After removal of the applied electric field, the polarization persists and a hysteresis is observed. Sophisticated ferroelectric organic materials are attractive, as they promise applications in the field of memory devices, [3,4] and organic electronic functions, coupled to ferroelectric behavior. [5-7] There are different mechanisms for organic ferroelectric effects that include hydrogen bonding, [8-10] liquid crystalline ordering, [11] charge-transfer complexes[12,13] and molecular rotation.[14,15] Among them, molecular rotation is most prominently described for polyvinylidene fluoride (PVF).[16] In PVF the uniformly unidirectional orientation of the polymer´s CF_2-groups creates a permanent polarization. This principle has been employed in other polymers, including polyamides, but little is known about conjugated polymers that attain ferroelectric properties by molecular rotation of some of their monomeric units. In materials that contain phenylene-ethynylene (PE) units, rotation of the aryl rings modulates their optical and electronic properties; their conformational behavior is well-investigated.[17-25] PEs are planar in the solid state and their structure is static (Figure 1a).

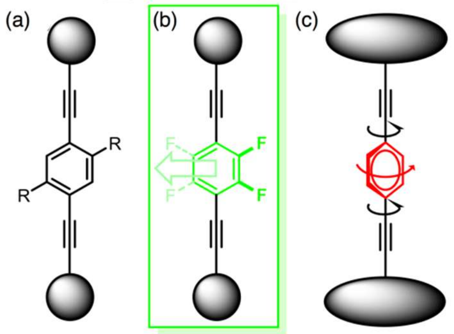

Figure 1. Fundamental situations for phenylene-ethynylene (PE)-based systems in the solid state. a) Static, b) dynamic and tunable by an external electric field, i.e. ferroelectric, c) dynamic, gyroscope-like. Molecular rotation is responsible for the generation of ferroelectric properties.

An exception to this rule was reported by Garcia-Garibay *et al*., who looked at PE units, shielded by two sterically demanding molecular stoppers (Figure 1c) and the pheny rings are free to rotate, both in solution, *but also in the solid state*. [26,27] They achieved thus molecular gyroscopes. The ability of a dipolar moiety to rotate will result in a macroscopic polarization upon application of an external electrical field but also in an immediate loss of the induced polarization upon removal of that field. To retain and switch the polarization, an appropriate but not excessive rotation barrier is required. Poly(*para*-phenylene-ethynylene) (PPE), show a small rotation barrier (~1 kcal mol^{-1}) [22] for the isolated molecule or in solution, but the barrier is higher in the solid state, due to the crystallinity of the material.[17-19] Consequently, employing PPEs backbones seems promising as switchable materials, where rotation is hindered but still possible upon exposure to an electric field. Here we present a ferroelectric PPE (Figure 1b), poled at room temperature with long lasting remanent polarization.

To introduce dipoles, difluorobenzene rings were integrated into the PPE chain (FF-HPPE). Three additional PPEs with different side chains but without dipolar moieties were also synthesized (Figure 2). FF-HPPE was obtained by standard Sonogashira coupling of diiodo-2,3-difluorobenzene and a suitable diyne (see SI). The other PPEs were also obtained in reasonable yield as yellow powders with moderate M_n and polydispersities. [28]

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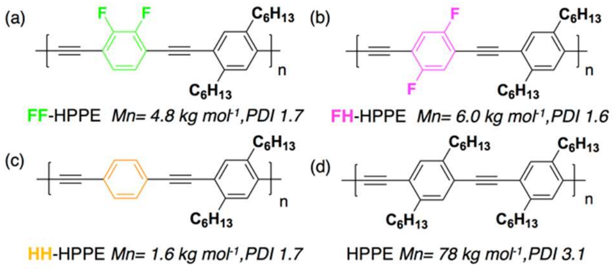

Figure 2. Molecular structures, number-average molecular weight (*Mn*), and polydispersity of PPEs employed in this study.

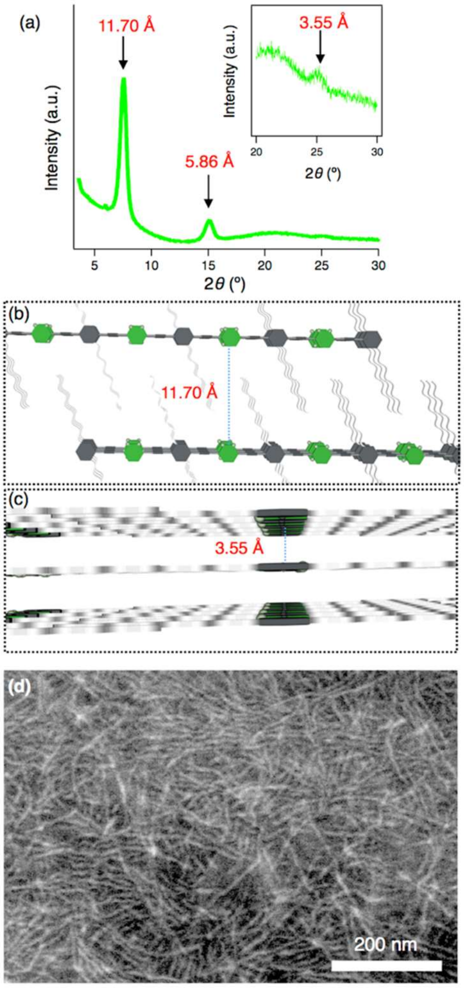

Figure 3. (a) XRD patterns of the film of FF-HPPE. X-ray source: CuKα. Insets show the expanded patterns in the range of 20º < 2θ < 30º. Top view (b) and side view (c) of suggested molecular packing of FF-HPPE. (d) SEM micrograph of the film of FF-HPPE.

Figure 3 and Figure S2 depict the powder diffraction patterns of the four crystalline PPEs. FF-HPPE, FH-HPPE and HH-HPPE show higher order than HPPE. While HPPE displays a lamellar packing, Other PPEs display interdigitated phases, as the main diffraction peak is shifted from 16.3 to 7.06, 10.0 and to 11.7 Å respectively. Interdigitation is further evidenced by a second diffraction peak at double of the angle. The diffraction signal at around 3.5-3.7 Å represents stacking distances in the PPEs. FF-HPPE, FH-HPPE and HH-HPPE show these signals. In the structure of FF-HPPE, the position of the difluorobenzene should be syntactic or atactic, canceling each other's dipoles by dipole-dipole interaction (one possible representation see Figure 3b,c). Thin films of FF-HPPE appear as a dense network of fibers (SEM, Figure 3d), each around 10 nm thick.

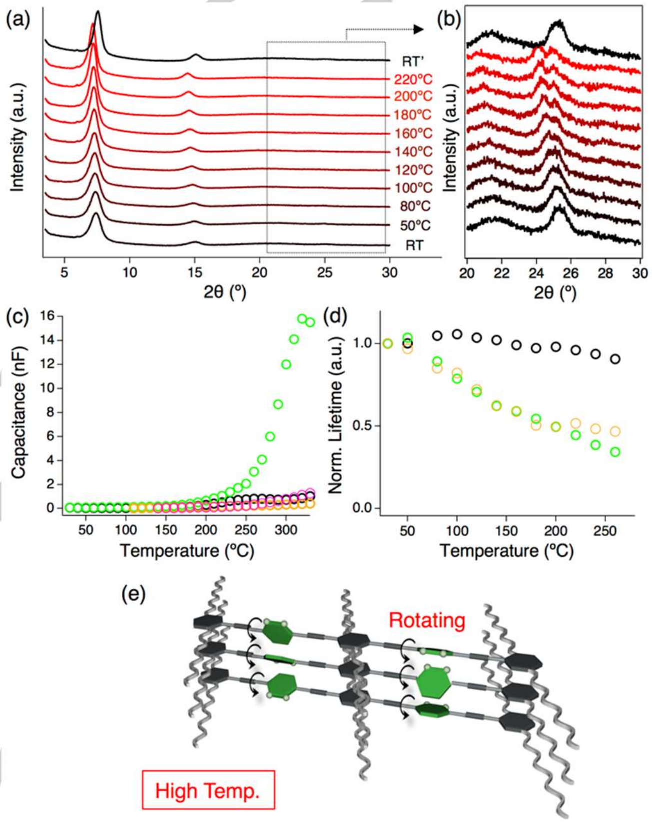

Figure 4. XRD patterns of a film of FF-HPPE (a) and their expansion on the range of 20° < 2θ < 30°(b) as a function of temperature (RT-220°C, black to red). RT and RT' means XRD pattern at room temperature before and after annealing. (c) Capacitance of FF-HPPE (green), FH-HPPE (pink), HH-HPPE (orange) and HPPE (black) as a function of temperature (RT-330 ºC) at 1Hz. (d) Relative photoluminescence lifetime of FF-HPPE (green) and HPPE (black) normalized by lifetime at RT. (e) a schematic illustration of FF-HPPE at high temperature.

Upon heating to 220 ºC, the structure of FF-HPPE changes (Figure 4a,b). The diffraction peak for the alkyl packing increases, moving to a lower angle. This is typical during annealing. [21,22] Contrary to this, the high angle peak at 25.1º, assigned to the polymer stacking, splits from 3.55 Å at room temperature into two peaks of decreasing intensity at 3.70 and 3.56 Å at 220ºC, pointing to the flip-flop motion between the canceling and aligning forms of dipoles at high temperature and rotation of the difluorobenzene units at higher temperature (Figure 4e), This is also observed for FH-HPPE, but not for other PPEs (Figure S3).

Flipping/rotation is confirmed by temperature dependent capacitance measurements[14,29]. The capacitance of FF-HPPE increases with temperature (Figure 4c, S4) and reaches its maximum at 320 ºC. The behavior is not observed for the other PPEs. The rotation barrier of 18.7 kcal mol^{-1} is estimated from the Arrhenius plot of the onset frequency of capacitance as a function of temperature (Figure S11). This value is slightly higher than the 10-15 kcal mol^{-1} of molecular gyroscopes reported by Garcia-Garibay.[26,27] The emission lifetime significantly decreases for FF-HPPE and HH-HPPE, when going to higher temperatures, but not for HPPE (Figure 4d, S5). The molecular rotation probably contributes to non-radiative decay. [30]

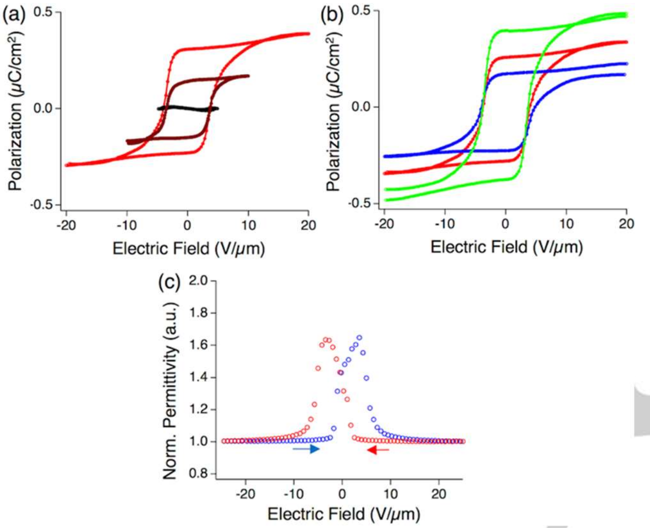

Figure 5. (a) *P-E* hysteresis curves vs. applied triangle electric AC field of ±5 (black), ±10 (brown) and ±20 V μm^{-1} (red) at 5 x 10^{-3} Hz. (b) Frequency dependent *P-E* curves at 2.5 x 10^{-3} (green), 5x 10^{-3} (red) and 10 x 10^{-3} Hz (blue). (c) Electric field dependent normalized permittivity of FF-HPPE film measured at an AC voltage of 100 mV at 100 Hz. The sweeping directions of blue and red curves are minus to plus and plus to minus, respectively.

The structural investigation and the electrical behavior of the FF-HPPE suggest a ferroelectric phase (Figure 5). A film (800 nm thick) was sandwiched between two ITO plates, and triangle AC voltage was applied at room temperature to pole the film (see SI). While no polarization hysteresis was found for HH-, FH- or HPPE derivatives (Figure S6) such hysteretic *P-E* characteristic were observed for FF-HPPE when the applied voltage exceeded ±5V μm^{-1}. At ±20 V μm^{-1} this behavior was much more significant and remanent polarization (P_r) of ~0.3 μC cm^{-2} was observed (Figure 5a). The *P-E* hysteresis was found at applied AC frequencies < 0.01 Hz (Figure 5b). A coercive electric field can be determined as 5.3 V μm^{-1} (from the hysteresis), but the remanent polarization cannot be determined, because it depends on the frequency. The molecular reorientation requires time to saturate and the pure remanent polarization can be obtained at a low-enough frequency. Consequently, a positive-up, negative-down (PUND), DC voltage technique for full saturation, was performed to obtain the correct value (Figure S9). The remanent polarization was determined to 0.45 μC cm^{-2}. This matches the result of DFT calculations, where 1.6 μC cm^{-2} was found, in particular when we take into account that the dipolar units will not align perfectly in the solid state. The remanent polarization of 0.45 μC/cm^2 and the coercive electric field of 5.3 V/μm compare well to that of other organic ferroelectrics, [8,9,14] although the response time is relatively slow (10^{-2}-10^{-3} Hz), related to the stacking distance. The ferroelectric property is mirrored in the electric field dependence of the permittivity (Figure 5c), where typical butterfly hysteresis was observed (Figure S9). [31]

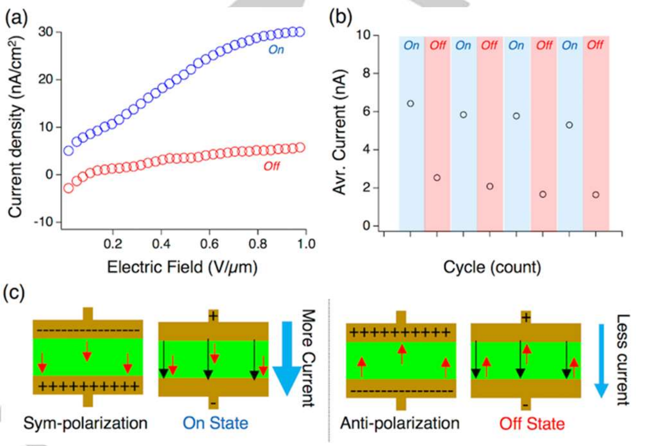

Figure 6. (a) Current density- electric field curve after the polarizing by -8 V (on state, blue) and -8 V (off state, red). (b) Averaged current under the electric field of 1.6 V/μm for 1 s after switching the polarization. (c) Schematic illustration of syn- and anti- polarizations.

The observed ferroelectric behavior relates to the dipolar moiety and the clamping of dipoles by the packing of neighboring PPE-chains. The molecular structure of PPE is vitally important for the ferroelectric behavior but provides at the same time semiconducting properties. PPEs have been employed as active layers in organic devices.[32-34] The optoelectronic properties of the three PPEs are shown in Figure S1 and Table S1,2. For all PPEs typical absorption and emission spectra were found. With a quantum yield of 0.15 in the solid state, FF-HPPE is quite fluorescent. FF-HPPE displays electrical conduction in MIM-diodes with ITO as contact material as the conduction of alkyl PPEs has been investigated earlier. [32,33] The ferroelectric phase in FF-PPE results in a modulation of the measured current (Figure 6b, SI). In sym-polarized devices, where the direction of the dipole moment aligns with the current direction (Figure 6c), the current density is considerably higher than in that of the anti-polarized one (Figure 6a). The mechanism is not clear but might stem from a change of an ohmic contact to a Schottky contact, [5] or to an induced electric field by polarization.[8] Current modulation in a simple memory device (Figure 6b) was proven but is limited, since the on/off ratio is an order of magnitude only. Nonetheless, the result suggests ferroelectric conjugated polymers to be useful for memory OLED, [6] memory OFET, [5] or high performance OPV. [7]
In conclusion, we prepared a ferroelectric PPE. *Ortho*-difluorinated benzenes in the PPE introduce dipole moments and the dipolar rings behave like molecular rotors at high temperature. The rotation barrier resulting from the PPE´s packing retains orientation of the molecular dipole moments at room temperature

and an electrical field induces a long lasting remanent polarization; FF-PPE behaves like a ferroelectric. The concept should be adaptable to any dipolar aromatic species incorporated into a poly(aryleneethynylene). Over all, this dynamic concept should deliver a rich harvest and add to the property-development of organic semiconductors for OLEDs, TFTs and memory devices.

Experimental Section

Synthesis and experimental details are described in supporting information.

Acknowledgements

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Keywords: Polymers• Molecular devices •Organic Ferroelectrics • Molecular Rotors

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Layout 1:

COMMUNICATION

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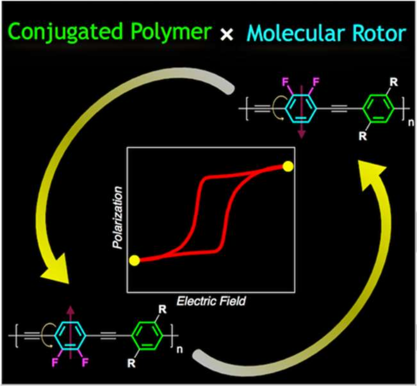

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