# Facile Doping of Anionic Narrow-Band-Gap Conjugated Polyelectrolytes During Dialysis**

*Cheng-Kang Mai, Huiqiong Zhou, Yuan Zhang, Zachary B. Henson, Thuc-Quyen Nguyen, Alan J. Heeger, and Guillermo C. Bazan**

Conjugated polyelectrolytes (CPEs) are defined by a backbone that contains a π-conjugated electronic structure with pendant ionic functionalities.[1] They are fascinating objects of study, as they combine the optical and charge transport properties of organic semiconductors with the possibility of modulating physical properties by electrostatic interactions. Water-soluble CPEs have found utility as optical reporters in biosensors and bio-imaging applications.[2] Furthermore, owing to their solubility in polar solvents, it is possible to fabricate multilayer optoelectronic devices in combination with neutral conjugated polymers. CPE interlayers have thus proven useful in organic solar cells,[3] organic light-emitting diodes,[4] and organic thin-film transistors.[5]

Cationic narrow-bandgap conjugated polyelectrolytes with a backbone containing alternating 4,4-bis-alkyl-4*H*-cyclopenta-[2,1-b;3,4-b′]-dithiophene and 2,1,3-benzothiadiazole structural units (Scheme 1) were recently reported.[6] For the specific case of PCPDTBT-Pyr+BIm4−, one observes unexpected n-type transport in thin-film field-effect transistors. It was proposed that the pendant cationic functionalities



**Scheme 1.** Structures of cationic narrow-band-gap CPEs PCPDTBT-Pyr+Br− and PCPDTBT-Pyr+BIm4−.

[*] Dr. C.-K. Mai, Dr. H. Zhou, Dr. Y. Zhang, Z. B. Henson,
Prof. Dr. T.-Q. Nguyen, Prof. Dr. A. J. Heeger, Prof. Dr. G. C. Bazan
Center for Polymers and Organic Solids
Department of Chemisty and Biochemistry, Materials, and Physics,
University of California
Santa Barbara, CA 93106 (USA)
E-mail: bazan@chem.ucsb.edu
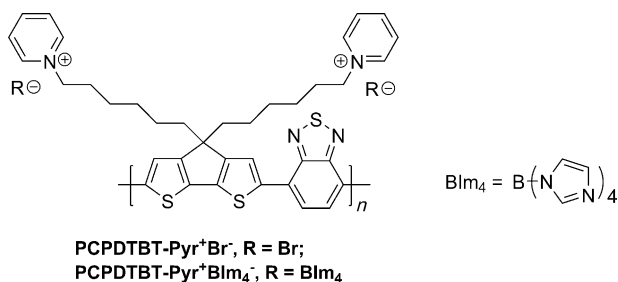Homepage: http://www.chem.ucsb.edu/bazangroup/home

lower both the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), thus stabilizing the radical anions in the conjugated backbones.

Herein we report a study on anionic counterparts of PCPDTBT-Pyr+BIm4− with charges provided by pendant sulfonate groups. These materials (Scheme 2) display a propensity to form cationic polarons, even by the simple action of dialysis, thereby yielding self-doped polymers.[7] Comparison against structurally related CPEs allows us to delineate structural features that facilitate this change in electronic properties.

The preparation of PCPDTBTSO3K is shown in Scheme 2. Alkylation of commercially available cyclopenta-dithiophene (CPDT) with 1,4-butanesultone under basic conditions, followed by bromination using *N*-bromosuccinimide (NBS), provides water-soluble monomer **1**. Suzuki coupling of **1** and commercially available bispinacolate **2** in a DMF/H2O solvent mixture affords the target PCPDTBTSO3K.[8] For purification, PCPDTBTSO3K was precipitated in acetone, filtered, washed with copious amounts of acetone and methanol, and subjected to dialysis in water for three days. The molecular weight cut off of the dialysis membrane is 3500–5000 Da. After drying under vacuum, the product is obtained as a dark blue solid. The ionic nature of PCPDTBTSO3K renders it soluble in water and insoluble in polar organic solvents, such as CH3CN, MeOH, DMF, and DMSO.

Exchange of the countercations in PCPDTBTSO3K was carried out with excess tetrabutylammonium bromide (TBABr) with the aim of improving solubility and facilitating characterization.[9] Purification by dialysis in water provided a new CPE, namely PCPDTBTSO3TBA, in which the original potassium countercations are replaced with more solubilizing tetrabutylammonium counterparts.[10] PCPDTBTSO3TBA can thus be dissolved in MeOH, DMF, and DMSO, and thereby enable determination of molecular weight by gel permeation chromatography in DMF. The number average molecular weight was determined to be about 8 kgmol−1. The low molecular weight most likely arises due to precipitation of PCPDTBTSO3K during the polymerization reaction.

The UV/Vis-NIR absorption spectra of PCPDTBTSO3K in water obtained before and after dialysis are provided in Figure 1. The spectrum of PCPDTBTSO3K before dialysis exhibits two main bands, centered at 410 nm and 670 nm, that are within the usual range for donor–acceptor copolymers and are characteristic for polymers with π-conjugated cyclopenta-[2,1-b;3,4-b′]-dithiophene-*alt*-4,7-(2,1,3-benzothiadiazole) backbones.[11] After dialysis, however, a broad, low-energy
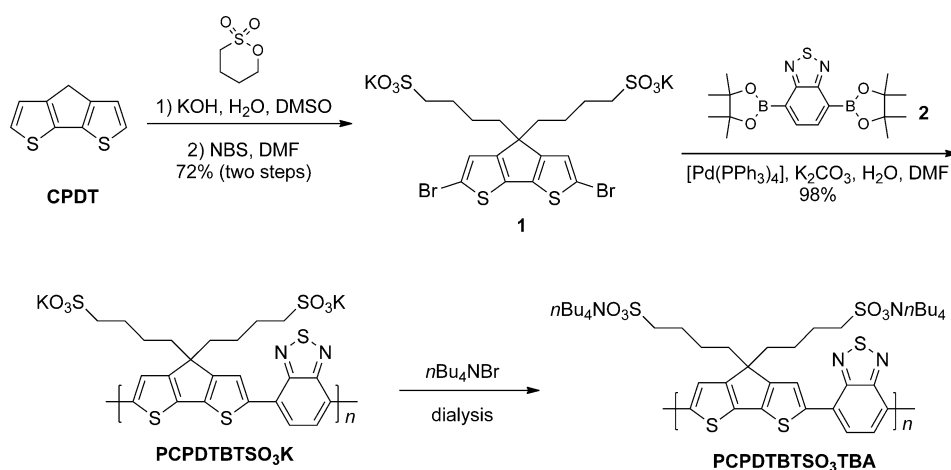
**Scheme 2.** Synthesis of narrow-band-gap conjugated polyelectrolyte PCPDTBTSO₃K, and the conversion into PCPDTBTSO₃TBA.

Because dialysis in deoxygenated water is not practical, we took advantage of the reversibility of the pH dependent doping–dedoping process, and conducted absorption measurements in deoxygenated solutions (Figure 3). First, KOH (20 equiv) was added to an aqueous solution of PCPDTBTSO₃K to achieve a low doping level (Figure 3a), and this solution was degassed with Ar for 15 min. Addition of a degassed solution of $H_2SO_4$ (100 equiv) under these conditions provides a solution with
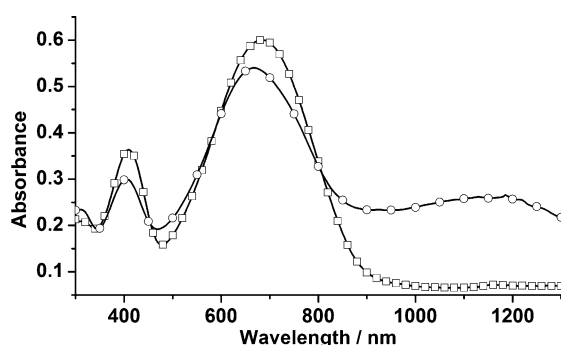


**Figure 1.** UV/Vis-NIR absorption spectra of PCPDTBTSO₃K in water (0.025 mg mL⁻¹), before dialysis (□) and after dialysis (○).



**Figure 2.** a) UV/Vis-NIR absorption spectra of PCPDTBTSO₃K in solution (1:1 H₂O:MeOH, 0.1 mg mL⁻¹) with 10 equiv HCl added (△) and with 10 equiv KOH added (□); b) EPR signals: after dialysis (○), with 10 equiv HCl added (△), and with 10 equiv KOH added (□).

transition is also observed that begins at about 900 nm and extends beyond 1300 nm. The energy range of this transition is reminiscent of those exhibited by polarons.[12] It is also relevant that a similar band is observed after addition of $I_2$ (Supporting Information, Figure S5).

The possible presence of polarons as indicated by the spectra in Figure 1 prompted us to investigate a possible doping mechanism. It was first determined that the contribution of the low-energy band to the total optical absorption of PCPDTBTSO₃K can be modulated by addition of acid or base. As shown in Figure 2a, the 1150 nm peak increases upon addition of 10 equiv HCl (relative to monomer units), and is absent when 10 equiv KOH are added. Electron paramagnetic resonance (EPR) measurements (Figure 2b) of PCPDTBTSO₃K (after dialysis) solution show a signal with narrow line shape (peak-to-peak line width $\Delta H_{pp} = 4.0$ G) and a g-value ($g = 2.0001$), consistent with the presence of unpaired electrons.[13] The intensity of this peak correlates with the band at 1150 nm, indicating that this optical transition is proportional to the number of free radical species.

Acid-catalyzed photo-oxidation in the presence of oxygen has been proposed to explain certain doping process of water-soluble polythiophenes with sulfonic acid side chains.[14]
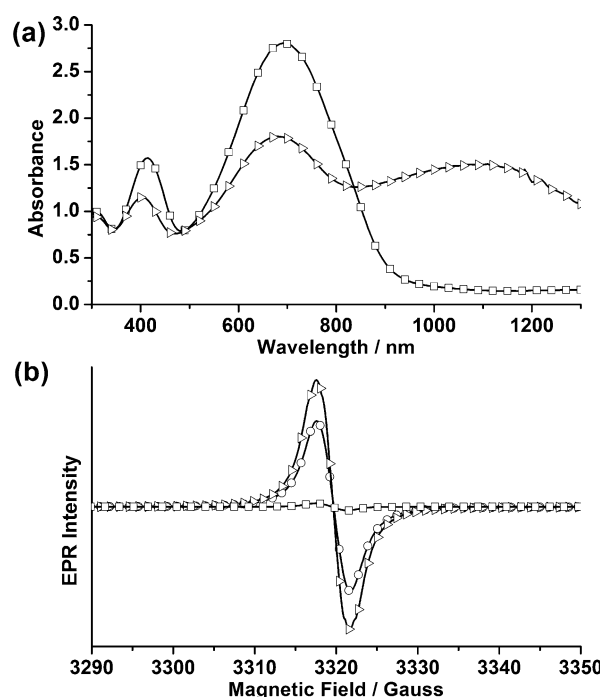
a very strong contribution from the low energy band. The presence of oxygen is therefore not a requirement for doping the polymer. The spectrum observed after mixing PCPDTBTSO₃K and $H_2SO_4$ without degassing exhibits a lower contribution from the low-energy band, which suggests possible instability toward oxygen for the very highly doped systems. An independent verification of the importance of protonation was carried out by "titrating" an aqueous solution of PCPDTBTSO₃K with $p$-toluenesulfonic acid ($p$-TsOH) under air (Figure 3b). $p$-TsOH addition leads to an increase of the polaronic peak, with a concomitant drop
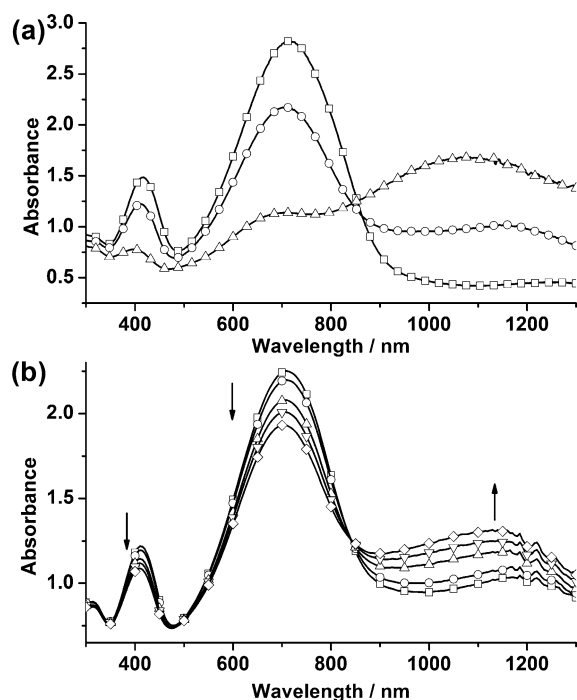
*Figure 3.* a) UV/Vis-NIR absorption spectra of PCPDTBTSO₃K in water (0.1 mg mL⁻¹) with 20 equiv KOH added (□), after acidification with 100 equiv H₂SO₄ under ambient conditions (○), and under careful degassed conditions (△); b) Absorption spectra during titration of PCPDTBTSO₃K in water (0.1 mg mL⁻¹) with *p*-TsOH (□ 0 equiv, ○ 1 equiv, △ 2 equiv, ▽ 5 equiv, ◇ 10 equiv).



*Figure 4.* UV/Vis-NIR absorptions of PCPDTBTSO₃TBA in different polar solvents (0.1 mg mL⁻¹): H₂O (□), MeOH (○), and DMSO (△).



*Figure 5.* UV/Vis-NIR absorptions of PCPDTBT-Pyr⁺BIm₄⁻ in 1:1 H₂O/ MeOH. □ Pristine; ○ after addition of 50 equiv HCl.

of the original bands. Protonic acids have been systematically studied as non-oxidizing dopants for conjugated polymers.[15] By analogy to previous studies on self-doped polymers,[7,14,16] we proposed that doping during dialysis proceeds via a mechanism that involves initial double protonation of one polymer backbone, followed by comproportionation with a non-protonated chain, ultimately leading both to the formation of polarons (radical cations), which are stabilized by the pendant sulfonate groups.[15] These observations tell us that the polymer can be doped exclusively by protonation via mechanisms previously established for self-doped polymers;[7,14,16] however, possible doping by oxygen under all circumstances cannot be ruled out.

Having access to PCPDTBTSO₃TBA allows us to examine how the nature of the medium influences the degree of doping.[17] The absorption spectra of PCPDTBTSO₃TBA after dialysis in different solvents are shown in Figure 4. Polaron absorption is observed in protic solvents (H₂O and MeOH), but not in an aprotic solvent (DMSO). In general, the pKa values of protic acids are higher in aprotic solvents, such as DMSO. For example, the p$K_a$ of CH₃SO₃H decreases by approximately three units when going from DMSO (p$K_a$ = 1.6) to water (p$K_a$ = −2.6).[18] It stands to reason that the sulfonate groups in DMSO behave in a manner similar to KOH in water, namely they inhibit protonation of the backbone, or deprotonate any sites, by virtue of being more basic in this medium.

Comparison of PCPDTBT-Pyr⁺BIm₄⁻ with PCPDTBTSO₃K and PCPDTBTSO₃TBA allows the back-

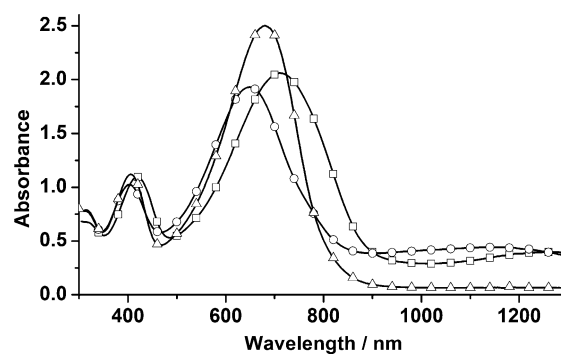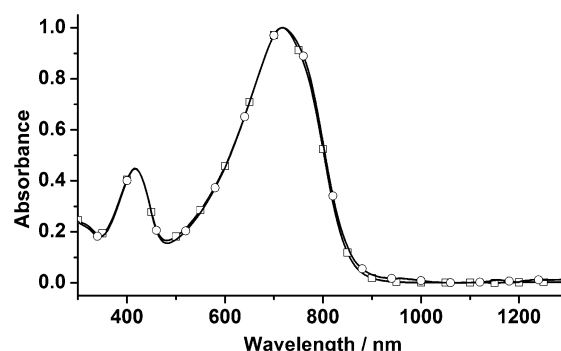bone structure to be kept constant and examine the role of electrostatic contribution by the pendant groups.[19] As shown in Figure 5, the absorption of PCPDTBT-Pyr⁺BIm₄⁻ is similar to that of PCPDTBTSO₃K in the presence of KOH. More importantly, no changes are observed when 50 equiv HCl are added to PCPDTBT-Pyr⁺BIm₄⁻. These data indicate that the anionic groups are important for stabilizing the (cationic) polaronic states and this most simply appears to be as a result of Coulombic stabilization.

As shown in Scheme 3, two anionic CPEs, PCPDTPhSO₃Na and PFBTSO₃Na, were prepared to probe which particular structural units in PCPDTBTSO₃K are most significant for the doping process. In PCPDTPhSO₃Na, the benzothiadiazole (BT) heterocycle in PCPDTBTSO₃K is replaced with a phenyl fragment, which is less electron-deficient.[20] In PFBTSO₃Na, the CPDT unit in PCPDTBTSO₃K, is replaced with the weaker donor fluorene fragment.[21] Detailed procedures for the synthesis, purification, and characterization can be found in the Supporting Information. Absorption spectra of PCPDTPhSO₃Na and PFBTSO₃Na, before and after dialysis, are provided in Figure 6. The spectrum of PCPDTPhSO₃Na (after dialysis) exhibits a broad transition extending from 600 nm to 1000 nm, while that of PFBTSO₃Na does not provide evidence of polaron absorption. These experiments highlight the importance of incorporating CPDT into the polymer backbone.

Frontier molecular orbital energy levels were estimated by using ultraviolet photoelectron spectroscopy (UPS) and
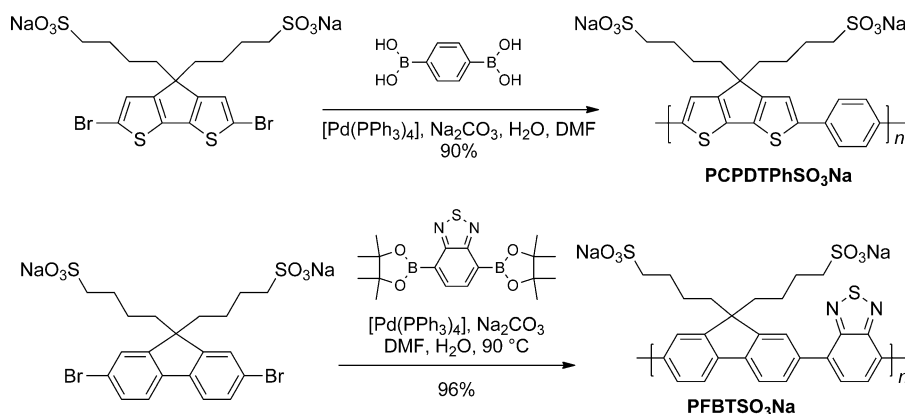
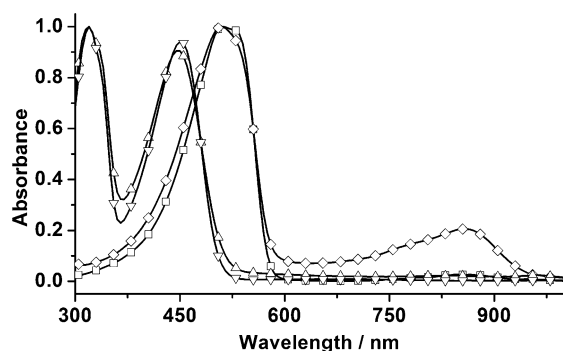**Scheme 3.** Synthesis and structures of conjugated polyelectrolytes PCPDTPhSO₃Na and PFBTSO₃Na.



**Figure 6.** UV/Vis-NIR absorption spectra of PCPDTPhSO₃Na and PFBTSO₃Na in aqueous solutions. PCPDTPhSO₃Na: □ before dialysis, ◇ after dialysis; PFBTSO₃Na: △ before dialysis, ▽ after dialysis.



**Figure 7.** Current–voltage plot of thin films: PCPDTBTSO₃K (□ after dialysis, $\sigma = 1.5 \times 10^{-3}$ S cm$^{-1}$), PCPDTBTSO₃K with 10 equiv HCl added (○, $\sigma = 1.2$ S cm$^{-1}$), PEDOT 4083 (Clevios VP. Al 4083, △, $\sigma = 2.7 \times 10^{-3}$ S cm$^{-1}$), and PEDOT PH (Clevios PH, ▽, $\sigma = 2.0$ S cm$^{-1}$).

polymers: polymers with higher IP values require stronger acids for doping.[15] Since PCPDTBTSO₃K-(TBA), PCPDTPhSO₃Na, and PFBTSO₃Na bear the same sulfonate side chains, these findings indicate that electron-rich heterocyles, CPDT in our case, which provide polymers with lower IP, should favor doping by dialysis.

Doping of conjugated polymers is known to increase electrical conductivity.[22] We thus measured the current–voltage response of PCPDTBTSO₃K thin films by adopt-
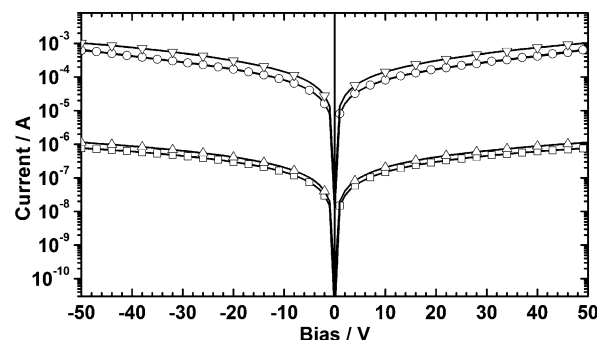
**Table 1:** Summary of frontier molecular energy levels [eV] obtained by UPS, UV/Vis-NIR absorption, and CV.

| Polymer | IP[a] | HOMO[b] | EA[c] | $E_g$[d] |
|---|---|---|---|---|
| PCPDTBTSO₃K | 4.87 | −4.83 | 3.49 | 1.38 |
| PCPDTPhSO₃Na | 4.92 | −5.11 | 2.78 | 2.14 |
| PFBTSO₃Na | 5.38 | −5.76 | 2.98 | 2.44 |

[a] From UPS measurements. [b] From CV measurements. [c] Estimated by using the IP value and the optical $E_g$. [d] Estimated from onsets of the absorptions of the undoped materials before dialysis.

cyclic voltammetry (CV). Experimental details can be found in the Supporting Information, and a summary of the most relevant findings is provided in Table 1. PCPDTBTSO₃K possesses the narrowest bandgap, lowest ionization potential (IP, and therefore highest HOMO energy level), and the largest electron affinity (EA). The IP of PCPDTPhSO₃Na (4.92 eV) is similar to that of PCPDTBTSO₃K (4.87 eV). PFBTSO₃Na has the broadest bandgap and highest IP (5.38 eV) among the three CPEs. These trends are consistent with the electronic properties of the structural units. Moreover, the observation that doping occurs for the materials with lowest IPs is consistent with previous reports on how protonic acids can function as non-oxidizing dopants for conjugated

ing a planar diode configuration, and the results are shown in Figure 7. Adding 10 equiv of HCl significantly improves the electrical conductivity of the PCPDTBTSO₃K obtained by dialysis, while adding 10 equivalent of KOH provides a non-conducting material, with a conductivity that is below the measurable limit of our experimental set-up ($< 10^{-12}$ S cm$^{-1}$, data not shown). These findings are consistent with the EPR measurements (Figure 2b). From a practical perspective, it is interesting to note that, as shown in Figure 7, the electrical conductivity of PCPDTBTSO₃K (after dialysis, $\sigma = 1.5 \times 10^{-3}$ S cm$^{-1}$) is comparable with a widely used commercially available conducting polymer, namely PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (Clevios VP. Al 4083, $\sigma = 2.7 \times 10^{-3}$ S cm$^{-1}$).[23] Post treatment with HCl, PCPDTBTSO₃K exhibits a conductivity ($\sigma = 1.2$ S cm$^{-1}$) similar to that of a more conductive version of PEDOT:PSS (Clevios PH, $\sigma = 2.0$ S cm$^{-1}$; Figure 7). This modulation of conductivity of PCPDTBTSO₃K, together with its low acidity (pH 7.56, 1.0 mg mL$^{-1}$ in water), renders it a promising material for applications in organic electronics.[24,25]

In conclusion, we designed and synthesized an anionic narrow-band-gap conjugated polyelectrolyte, PCPDTBTSO₃K. Ion exchange of charge compensating cations, that is, K versus TBA, can be used to modulate

solubility and thereby aid structural characterization. Purification by standard dialysis provides a material that is intrinsically doped, as determined by optical absorption and EPR spectroscopies. Electrical conductivity measurements are also consistent with a doped material. Protic solvents that lower the basicity of the sulfonate groups are important for favoring backbone doping (as opposed to sulfonic acid formation). That PCPDTBTSO$_3$K(TBA) is doped under acidic conditions that leave PCPDTBT-Pyr$^+$BIm$_4^-$ unperturbed highlight the importance of the pendant group charges. We presume that the anionic groups stabilize the positive charge on the backbone by electrostatic interactions. Moreover, comparison of PCPDTBTSO$_3$K(TBA) with PCPDTPhSO$_3$Na and PFBTSO$_3$Na allows us to confirm that doping is favored by the presence of CPDT. This fragment is known to be a strong donor in the construction of narrow band gap conjugated polymers and implies that it exhibits a low ionization potential. Given the wide number of related structures, a new diversity of easy to prepare conducting polymers can be envisioned. Moreover, the intrinsic conductivity renders these doped CPEs as promising materials for organic electronics.[24, 25]

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