

**CHEMPLUSCHEM**

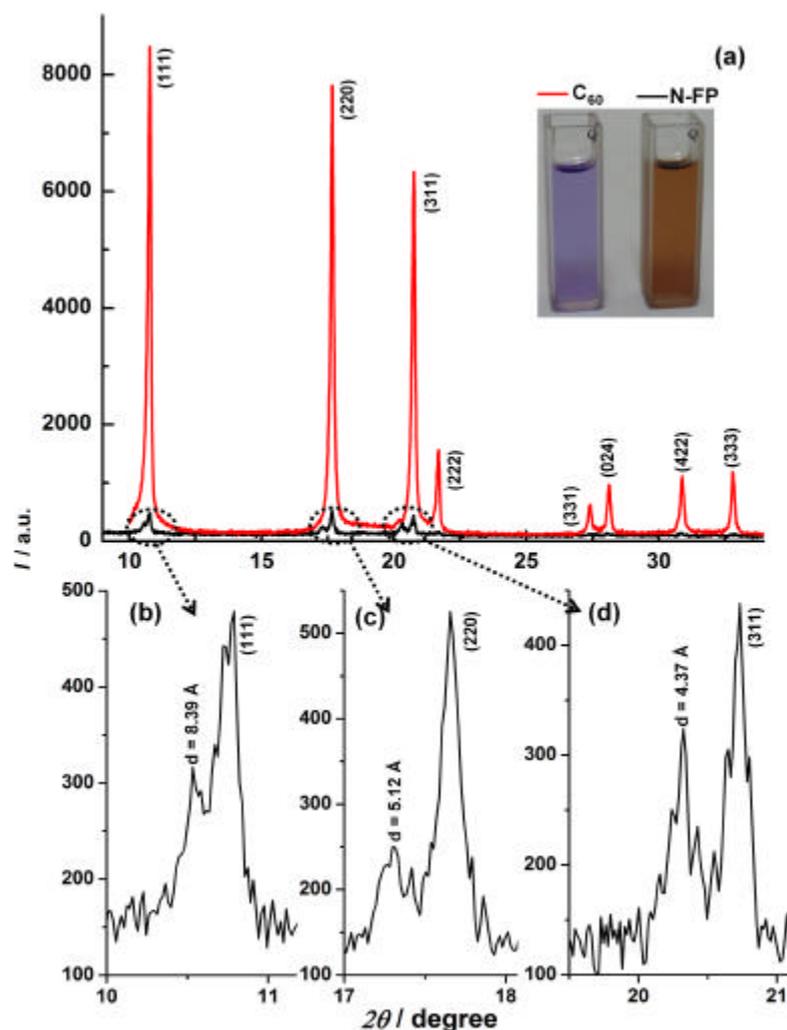
## Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2012

### **Color in Poly(3,4-ethylenedioxythiophene) with Profound Implications for Electronic, Electrochemical, and Optical Functions**

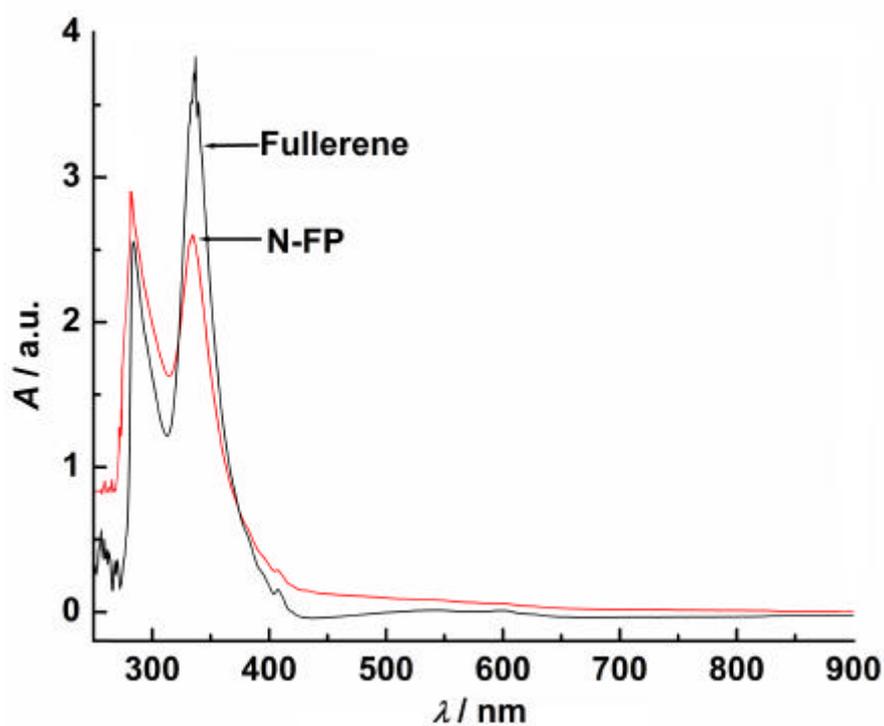
Rambabu Sydam and Melepurath Deepa\*<sup>[a]</sup>

[cplu\\_201200035\\_sm\\_miscellaneous\\_information.pdf](#)

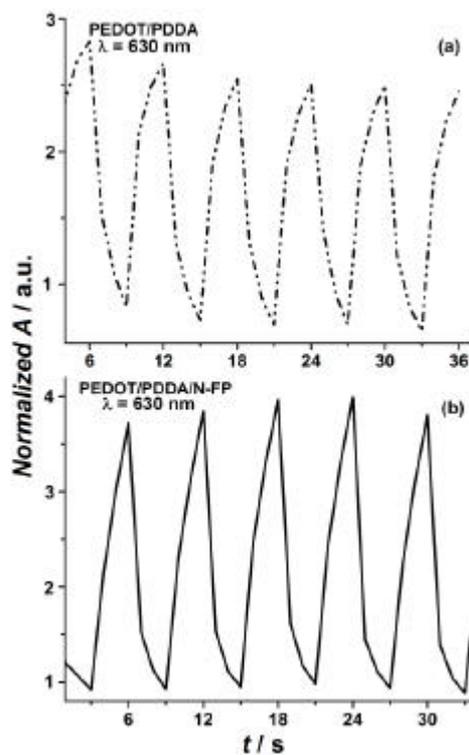


**Figure S1** X-ray diffractograms of (a) neat fullerene and N-methyl fulleropyrrolidine (N-FP), (b), (c) and (d) are enlarged views of the XRD patterns of N-FP showing the emergence of new d lines in addition to the contributions from neat  $C_{60}$ ; with hkl enclosed in parentheses.

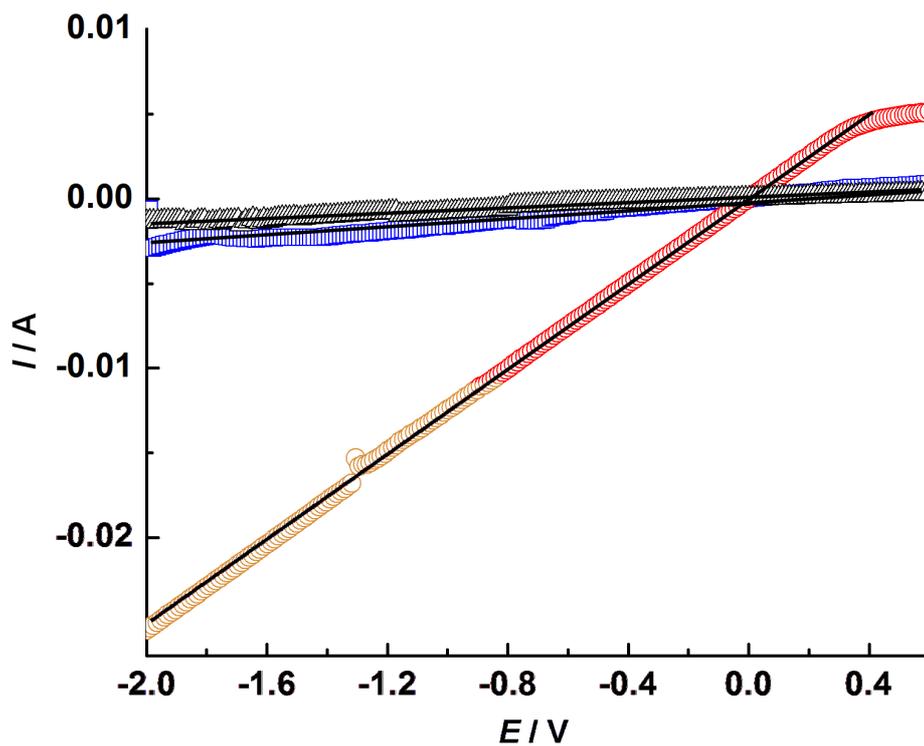
X-ray diffractograms of a neat fullerene and N-methyl fulleropyrrolidine are shown in Figure S1a. Neat fullerene shows three high intensity distinctive peaks at  $d = 8.20$ ,  $5.01$  and  $4.28$  Å corresponding to (111), (220) and (311) reflections of face centered cubic (fcc) lattice of  $C_{60}$  molecules which concurs well with the PDF file number: 82-0505. In addition, five low intensity lines are also observed for neat fullerene, which are not observed for the derivative. Albeit an overall decrease in the intensity of the peaks, the derivative: N-methyl fulleropyrrolidine, also showed the main diffraction lines at  $d = 8.22$ ,  $5.01$  and  $4.28$  Å, indicating that the fcc crystal structure of neat fullerene is preserved upon derivatization. However, the enlarged views of these peaks, shown in Figure S1b, c and d, reveal that these three main peaks have split with additional components at  $d = 8.39$ ,  $5.12$  and  $4.37$  Å, suggestive of some alterations at the lattice level. The modified XRD pattern is an indirect indicator of successful derivatization.



**Figure S2** Absorption spectra of neat fullerene and N-fulleropyrrolidine in toluene.



**Figure S3** Color-bleach kinetics of (a) PEDOT/PDDA and (b) PEDOT/PDDA/N-FP films at a  $\lambda_{max(ox)}$  = 630 nm; all measurements performed under a square wave pulse of  $\pm 2.5$  V with a step time of 3 s in 1-butyl-1-methyl pyrrolidinium trifluoromethanesulfonate.

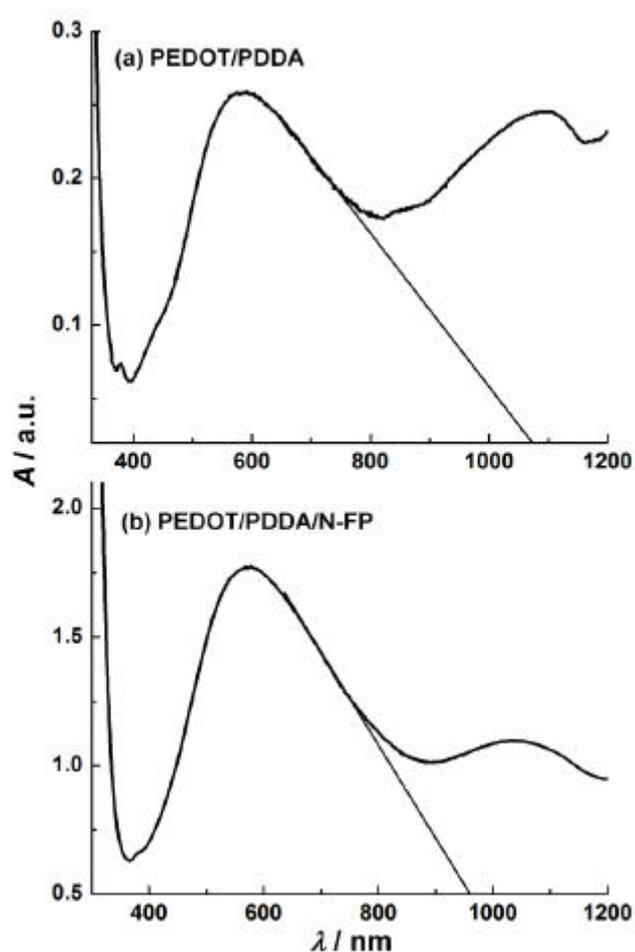


**Figure S4** *I-V* characteristics of PEDOT/PDDA ( $\Delta$ ), PEDOT/PDDA/N-FP ( $\circ$ ) and conventional PEDOT ( $\square$ ) films in a configuration wherein the sample is sandwiched between two conducting electrodes ( $\text{SnO}_2\text{:F}$  and stainless steel).

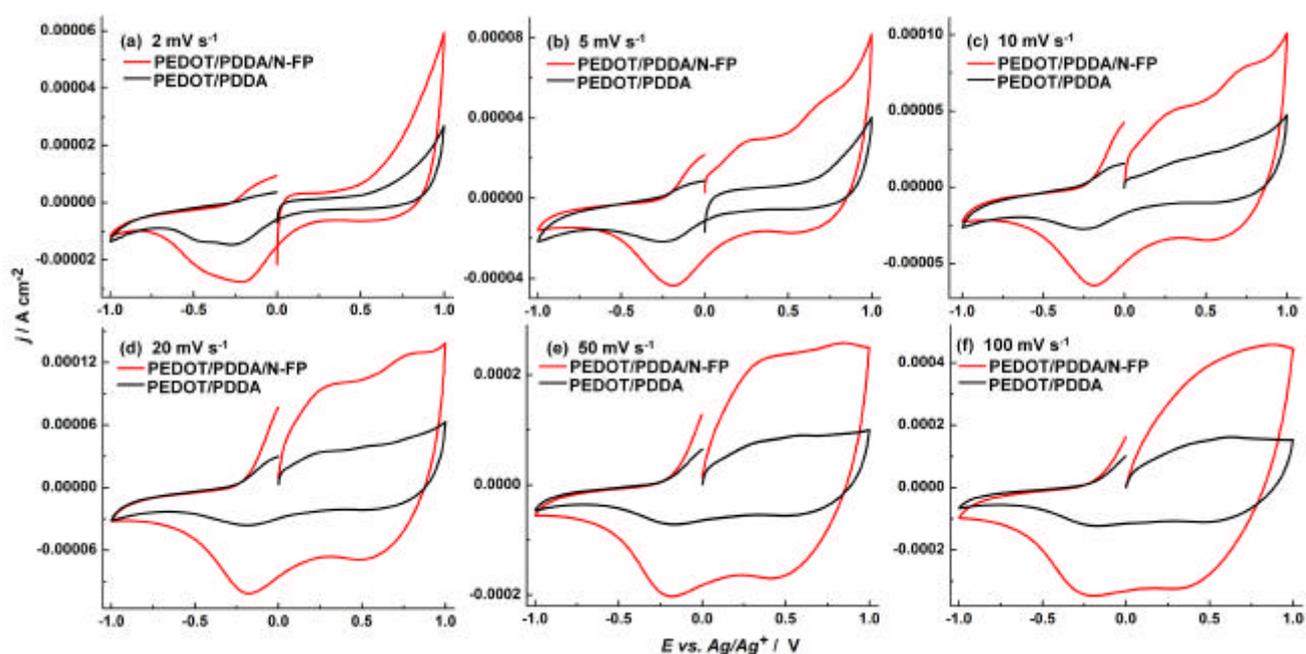
Bulk conductivity of PEDOT/PDDA, PEDOT/PDDA/N-FP and conventional PEDOT films was determined by using spring loaded point (stainless steel) contacts on the film surface, and measuring *I-V* characteristics by linear sweep voltammetry (LSV). Conductivities were determined using the slopes of the *I-V* curves and applying Ohm's law, by applying equation (1).

$$s \text{ (S cm}^{-1}\text{)} = (I/V) \times d/a \quad (1)$$

In equation (1), *I/V* is the slope of the *I-V* curve and is equal to the reciprocal of resistance and *d* is the thickness of the sample and *a* is the area of contact.



**Figure S5** Absorption edges for determination of band gap of as fabricated (a) PEDOT/PDDA and (b) PEDOT/PDDA/N-FP films.



**Figure S6** Cyclic voltammograms of PEDOT/PDDA and PEDOT/PDDA/N-FP films recorded within a voltage window of  $\pm 1.0$  V at scan rates of (a) 2, (b) 5, (c) 10, (d) 20, (e) 50 and (f) 100  $\text{mV s}^{-1}$  in the ionic liquid: 1-butyl-1-methyl pyrrolidinium trifluoromethanesulfonate.

Cyclic voltammograms of PEDOT/PDDA and PEDOT/PDDA/N-FP films were compared within a voltage window of  $\pm 1$  V at different scan rates and these plots are shown in Figure S6. At a scan rate of  $5 \text{ mV s}^{-1}$ , the difference between the redox activities of the two films becomes apparent. For the PEDOT/PDDA/N-FP film, a broad oxidation peak is registered at  $+0.27$  V ascribable to the egress of cations from the polymer film and the second oxidation peak seen at  $+0.69$  V is attributed to further oxidation, as the positive charges on the polymer chain surpass the number of bound anions and therefore electroneutrality is attained by compensation with trifluoromethanesulfonate ions of the electrolyte. In the reverse scan, the reduction peak at  $-0.19$  V corresponds to the movement of the electrolyte anions out of the film matrix leading to the formation of neutral PEDOT. In case of the PEDOT/PDDA film, no oxidation peak was observed at any scan rate and only a single reduction peak was seen at  $-0.23$  V, corresponding to the formation of neutral PEDOT. At any given scan rate, the area under the voltammogram is larger for the PEDOT/PDDA/N-FP film as compared to the PEDOT/PDDA film, which confirms that N-methyl fulleropyrrolidine, increases the charge storage capacity of PEDOT/PDDA film during redox switching. The response of both films shows a capacitive behavior at high scan rates of 50 and  $100 \text{ mV s}^{-1}$ . CV plots of PEDOT/PDDA however do not reflect the role of PDDA in controlling the optical behavior of PEDOT, as the CV curve obtained herein is quite similar to cyclic voltammograms obtained in the past for PEDOT films doped by conventional anions.<sup>[1]</sup> This indicates that although the optical absorption or band gap of the as-fabricated PEDOT/PDDA film is different from that of conventional PEDOT, nonetheless, the film does undergo oxidation and reduction in potential ranges similar to that shown by PEDOT doped with perchlorate ions.<sup>[1]</sup>

#### Assembly of quantum dot solar cells and characterization

A homogeneous and smooth  $\text{TiO}_2$  (anatase phase, particle size  $< 25$  nm, Aldrich) suspension was prepared in ethanol, by mixing  $\text{TiO}_2$  (1 g) in ethanol (5 mL). The resulting white formulation was coated on FTO coated glass using a doctor blade method and annealed at  $150^\circ\text{C}$  for 40 minutes to enable evaporation of the solvent and adherence of  $\text{TiO}_2$  to the substrate. CdS quantum dots (QDs) were deposited on the  $\text{TiO}_2$  coated glass electrodes by successive ionic layer absorption and reaction (SILAR) method.<sup>[2]</sup> The  $\text{TiO}_2$ /FTO electrode was sequentially immersed in four different beakers for about 30 s immersion time, in each solution. The first dipping solution contained aqueous  $\text{Cd}(\text{CH}_3\text{COO})_2$  (0.1 M, Merck) which, was followed by an ultrapure water rinse to remove superfluous acetate. The film was then immersed in aqueous  $\text{Na}_2\text{S}$  (0.1 M, Merck), and again followed by a water dip to remove the surplus sulfide. The immersion cycle was repeated ten times. The resulting films were yellow and were referred to as CdS/ $\text{TiO}_2$  electrodes. Quantum dot solar cells were assembled by using a CdS/ $\text{TiO}_2$  electrode as the photoanode, a PEDOT film (PEDOT/PDDA/N-FP or PEDOT/PDDA or conventional PEDOT (doped by camphorsulfonate ions)) as the counter electrode and aqueous  $\text{Na}_2\text{S}$  (0.1 M) as the electrolyte.  $I$ - $V$  characteristics were measured using a Newport Oriol 3A solar simulator with a Keithley model 2420 digital source meter. A 450 W Xenon arc lamp with an irradiance of  $100 \text{ mW cm}^{-2}$  of Air Mass (AM) 1.5 was used as the light source; the spatial uniformity of irradiance was confirmed by calibrating with a  $2 \text{ cm} \times 2 \text{ cm}$  Si Reference Cell traceable to NREL and re-confirmed with a Newport power meter.

**Table S1** Solar cell parameters for cells with CdS/ $\text{TiO}_2$ - $\text{Na}_2\text{S}$ -PEDOT configuration

Counter Electrode	$V_{oc}$ (mV)	$J_{sc}$ ( $\mu\text{A cm}^{-2}$ )	$FF$ (fill factor)	$\eta$ (Efficiency, %)
PEDOT/PDDA	570	145	63	0.05
PEDOT/PDDA/N-FP	635	740	88	0.42
Conventional PEDOT	632	655	73	0.30

#### References

- [1] A. Kumar, D. M. Welsh, M. C. Morvant, F. Piroux, K. A. Abboud, J. R. Reynolds, *Chem. Mater.* **1998**, *10*, 896-902.  
 [2] C. X. Guo, H. B. Yang, Z. M. Sheng, Z. S. Lu, Q. L. Song, C. M. Li, *Angew. Chem.* **2010**, *49*, 3014–3017.