Highly Soluble Polyoxyethylene-Perylene diimide: Optical, Electrochemical and Photovoltaic Studies

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Summary: The synthesis and optical properties of a new dye molecule [PERKAT] were reported. The molecular structure of PERKAT was characterized by FT-IR and ^{1}H NMR. Optical properties of PERKAT were investigated by UV-Vis absorption, fluorescence spectroscopy. The effect of the solvent polarity on the spectral characteristics has been investigated in five common organic solvents of different polarity. PERKAT is highly soluble in common organic solvents such as chloroform, dichloromethane due to the polyoxyethylene chains. The fluorescence quantum yields of PERKAT in all solvents is very low (10^{-2} -10^{-3}). Cyclic Voltammetry (CV) analysis was performed to determine the HOMO and LUMO energy levels of the PERKAT. PERKAT was used as electron acceptor material in organic solar cell.

Introduction

Perylene diimide (PDI) derivatives are highly versatile molecules, which attract a great interest owing to their applications such as organic solar cells (OSC), organic light emitting diodes (OLED), organic field effect transistors (OFET) [1-7]. At present, most successful photovoltaic devices are based on semiconducting materials such as silicon, but fabrication cost of these devices is very high. In recent years organic dye sensitized solar cells (DSSCs) have attracted considerable attention [8-10]. PDI derivatives were used for DSSCs. These molecules are inexpensive and easily accessible optoelectronic fluorescent pigments [11]. PDIs have been studied due to their high molar absorptivity, high fluorescence quantum yields together with excellent photochemical and thermal stability [12-16].

PDIs suffer from practical problems such as poor solubility and aggregation [17]. Different synthetic methods to prepare perylene derivatives with improved solubility have been reported [18]. Synthesis of highly soluble perylene diimide derivatives is very important for process ability and for the preparation of their thin films to be used in photo-electronic applications such as OSC, OLED and OFET, spectroscopic investigation and purification [19]. Soluble perylene dyes can be obtained by the introduction of solubility-increasing groups such as t-butylaryl or long-chain secondary alkyl groups (swallow-tailed substituents) at the nitrogen atoms [20].

We report here the detailed synthesis and characterization of perylene diimide shown in scheme 1. The new perylene diimide described here possess polyoxyethylene substituent group. Polyoxyethylene chains were chosen in order to increase solubility of molecule and improve film forming capacity. We have investigated UV-Vis absorption and steady state emission characteristics of the dye molecule related to medium effects. It has been used series of solvents which differ in their polarity. Furthermore, the optical, electrochemical, and photovoltaic properties of perylene diimide molecule were investigated.

Result and Discussion

Optical Properties of PERKAT

UV-Vis absorption spectra of the PERKAT dye taken in chloroform, benzonitrile, toluene and tetrahydrofuran solutions exhibit almost the same absorption properties in the visible spectrum located between 400-600 nm corresponding to π– π^* singlet transition reported for the perylene diimide but absorption bands are different in methanol. It is reported that long wavelength absorption band in polar solvents shows charge transfer character from electron-rich chain to imide carbonyls [23]. Fig. 1 shows the UV-Vis absorption spectra of PERKAT in various solvents. Absorption data are listed in Table-1.

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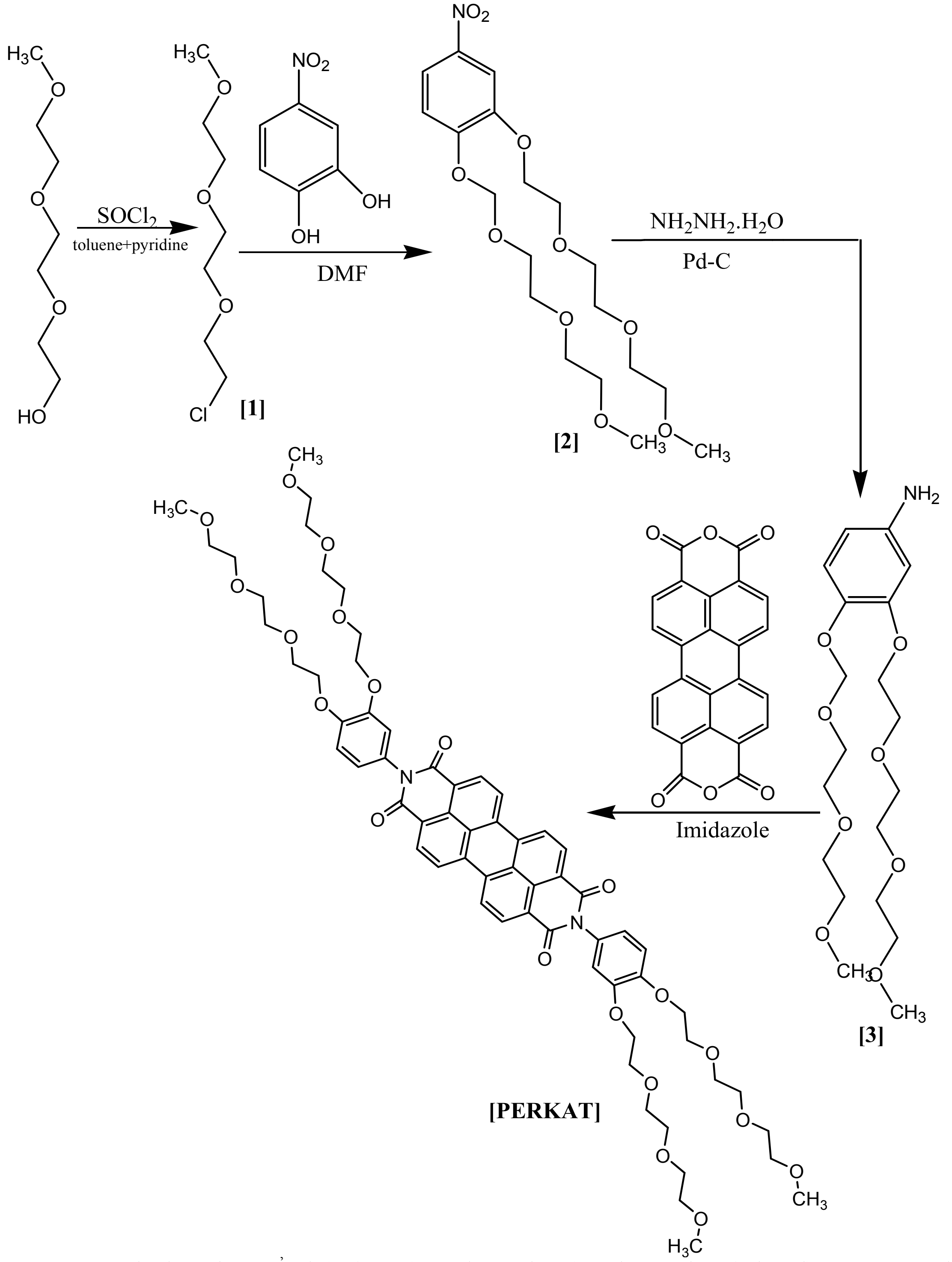

Scheme 1: Synthesis of N,N'-Bis(4-{2-[2-(2-methoxyethoxy) ethoxy]ethoxy}phenyl)-3,4:9,10-perylene tetracarboxydiimide [PERKAT].

Perylene diimide dyes show generally characteristic absorption peaks for the perylene diimide at 458, 490, 526 nm, which are denoted to their (0,2), (0,1), and (0,0) electronic transitions, respectively. These absorption peaks are matched by the corresponding emission peaks at 540, 576, 624 nm, respectively. Changing the solvents from chloroform to methanol causes a red shift in absorption spectra. The spectra are bathochromatically shifted as the solvent polarity increases, indicating an excited state that is more polar than the ground state [24]. The emission spectra of PERKAT fulfill the mirror image conditions to the absorption spectra in solutions. No clear substituent effect of polyoxyethylene on perylene diimide normalized emission spectra is observed, as given in Fig. 2. Since the two nitrogen positions at the imides are node in π orbital, substitution of the side chain with different moieties does not change the electronic structure of the perylene diimide molecule [25]. It is obvious that the polyoxyethylene chain length has no influence on the absorption spectra in solution and is due to the nodes at the imide nitrogen. Two emission peaks were observed at dilute solutions. The fluorescence intensity in benzonitrile solvent is higher than others. Whereas fluorescent perylene-3,4,9,10-tetracarboxylic-bis-N,N′-dodecyl diimide (N-DODEPER) shows high fluorescent quantum yield of Φ_f=1. PERKAT is non-fluorescent. The emission spectra of PERKAT were taken at λ_{exc}=485 nm and the relative fluorescence quantum yields were determined in various solvents. The fluorescence quantum yields (Φ_f) in dilute solutions of PERKAT have been measured with DODEPER in chloroform used as reference. Table 1 summarizes the Φ_f values which are low (0.0041 in toluene, 0.0027 in chloroform, 0.0016 in tetrahydrofuran, 0.014 in benzonitrile, 0.0014 in methanol). The low fluorescence quantum yields in various solvents can be attributed to the re-absorption of emitted photons and the self-quenching due to the intra and intermolecular interactions [27]. Also, the polyoxy-chains may be quench the fluorescence intensity. As the dielectric constant increases, the fluorescence quantum yield decreases [28].

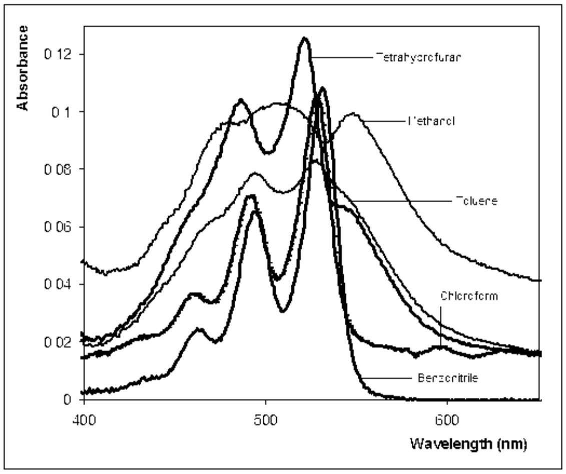

Fig. 1: UV-Vis absorption spectra of PERKAT in different solvents.

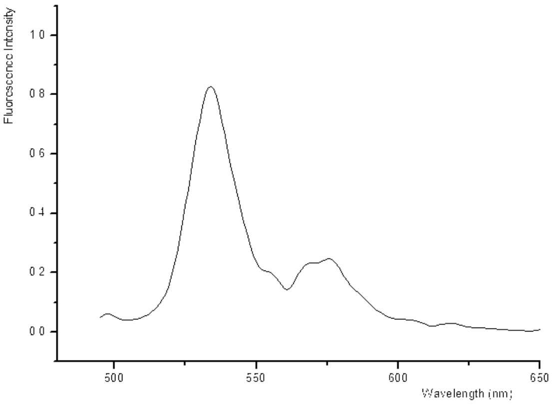

Fig. 2: Normalized fluorescence spectrum of PERKAT in chloroform.

We have examined fluorescence emission quenching of synthesized PERKAT by P3HT and calculated the fluorescence quenching rate constants by using Stern–Volmer equation [29].

$I_o/I=1+ kq \ x \ \tau_o x \ [Cq]$ (1)

where I and I_o are fluorescence intensity of P3HT in the absence and presence of quencher, kq is quenching rate constant, τ_o is fluorescence lifetime of polymer in the absence of quencher, [Cq] is concentration of quencher in solution. P3HT has attracted a lot of attention as a donor material. The fluorescence emission quenching of polymer by PERKAT ions is given in Fig. 3. After adding PERKAT solution, intensity of polymer solution decreased. Fluorescence quenching rate constant calculated as $2.2x10^{13}$. High quenching rates indicate towards the tendency of electron transfer process.

Cyclic Voltammetry Measurements

Cyclic Voltammetry measurements performed for spectroelectrochemistry experiments of the PERKAT dye in acetonitrile containing 0.1 M $TBAPF_6$ were shown Fig. 4. The perylene compounds show two reversible one electron reduction peaks [30]. First reversible reduction wave was observed in the range of -0.38/ -0.42 V and the second reduction potential was observed in the range of -0.57/-0.62 V . The reduction mechanism for the perylene diimide derivatives is known that electron transfer processes forms a radical anion occurs by the addition of an electron to the lowest LUMO and then the dianion with addition of a second electron to the same orbital [24]. The measured redox potentials for the PERKAT are listed in Table 2. In order to calculate the LUMO energy level of PERKAT with respect to the vacuum level, the redox potentials were calibrated to the ferrocene/ferricenium redox couple which has a calculated absolute energy of -4.8 eV [22]. One reversible oxidation wave, indicating the stable radical cation, was observed. The oxidation wave at 1.64 V for PERKAT corresponds to the oxidation of the perylene ring attached to the phenyl group to the radical cation. Generally the redox potentials of PDIs show the similarities unless substituted from perylene core. Redox behavior of the perylene diimide molecules is not affected significantly by N-substituent [31]. The calculated energies of the HOMOs and LUMOs of the PERKAT were given in Table 2. The LUMO energy level was calculated as -3.98 eV. The optical band gap value (E_g) was calculated as 2.37 eV. HOMO energy level have been found as -6.35 with formula $E_{HOMO} = E_{LUMO} - E_{gap}$.

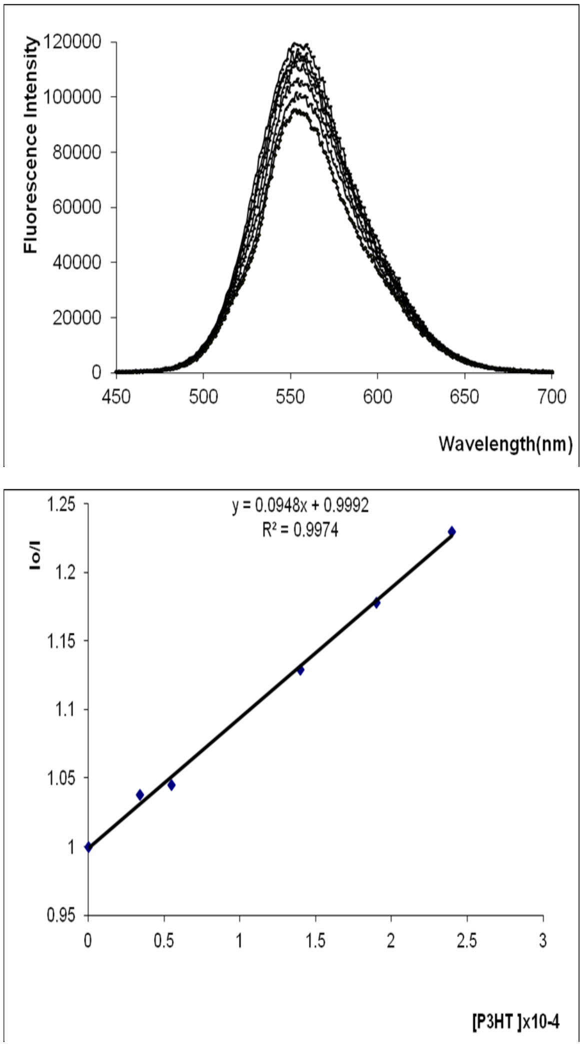

Fig. 3: Fluorescence emission quenching of polymer by PERKAT.

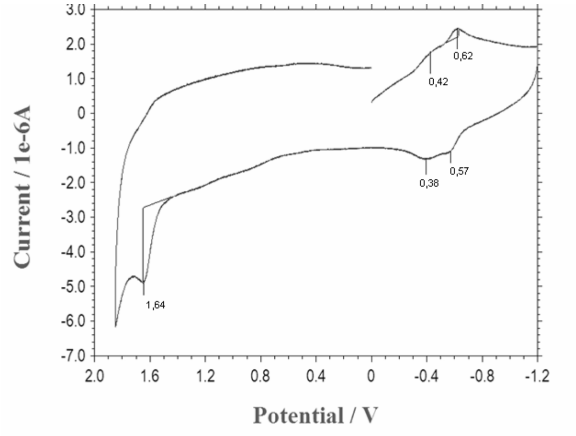

Fig. 4: Cyclic voltammogram at a glassy carbon electrode of PERKAT (1 mM) in MeCN containing 100 mM [TBA][PF6] and ferrocene as an internal electrode (E = 0.45 V).

Semi-empirical calculations were done for the characterization of three-dimensional structure and followed by single point CI configuration using Hyperchem Package Version 8.0 computational software. Fig. 5 shows the optimized structure and HOMO-LUMO energy densities of PERKAT dye. It is determined that both HOMO and LUMO levels have the charges localized on the same region of the perylene ring. Electron density of the ground and first excited state of PERKAT dye is distributed along ─C=C─C= linkage of the conjugated rings. These accumulation leads to a reduced angle between perylene plane and epoxy chains. Electron distribution in both ground and excited states of the dye restricts an effective electron injection to conjugated polymer in photovoltaic applications leading to low photon-to-electric conversion efficiency.

Photochemical Degradation and Thermal Stability

Photo-stability of PERKAT has been determined by following fluorescence intensity of the compound on the PTI spectrophotometer under Xe lamp irradiation for 1 h. It does not cause any decline on fluorescence intensity in chloroform solution.

It is known that perylene molecules are photo-stable. According to TGA, curve for PERKAT molecular structures decompose above 400°C and they show mostly two–step weight losses Fig. 6. The first one corresponds to loss of polyoxyethylene group attached to nitrogen atoms. The second step occurs due to aromatic ring degradation at above 600°C.

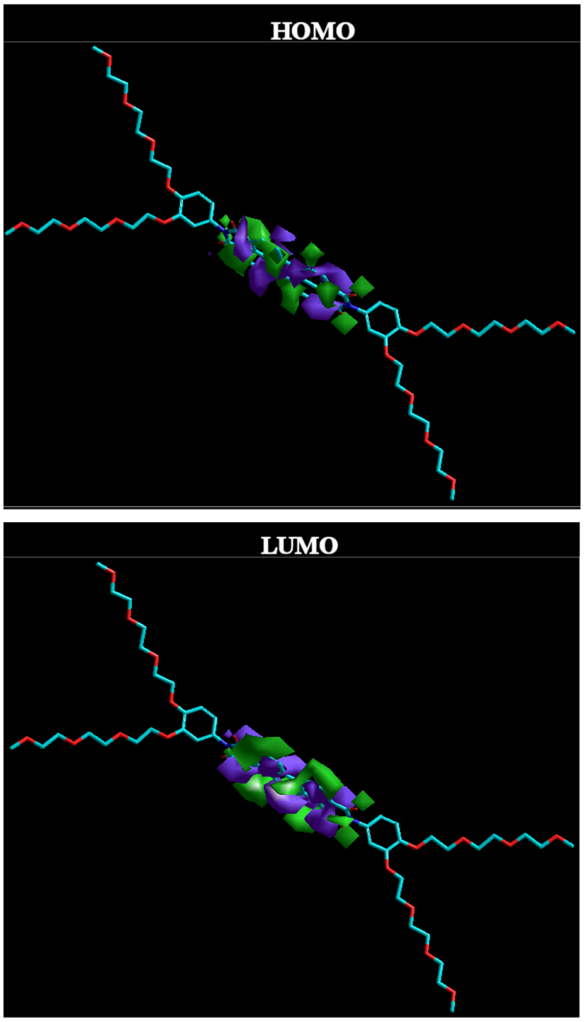

Fig.5: Schematic representation of the HOMOs and LUMOs of PERKAT

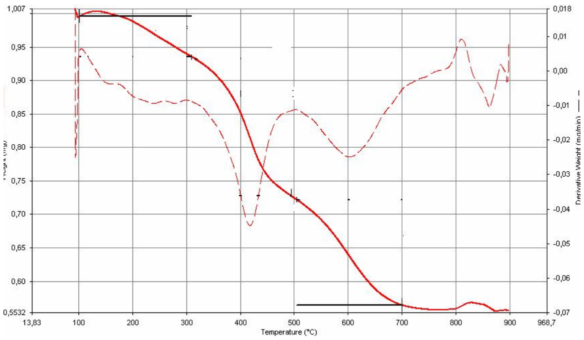

Fig. 6: TGA curve of N,N'-Bis(4-{2-[2-(2-methoxyethoxy) ethoxy]ethoxy}phenyl)-3,4:9,10-perylene tetracarboxydiimide [PERKAT]

Photovoltaic Performance

Fig. 7 shows the current-voltage (I-V) characteristics of the device under the dark and illumination with AM 1.5 global radiation and 100mW/cm^2 light power.

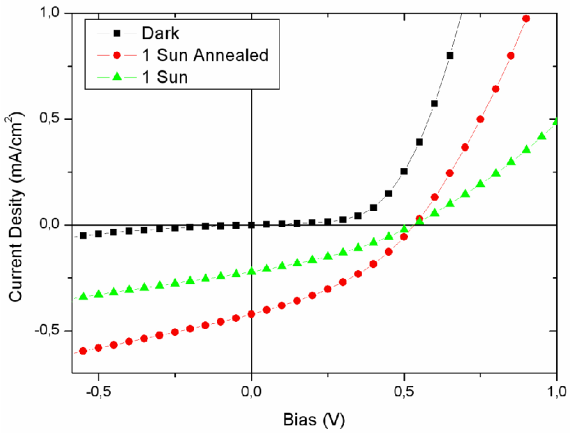

Fig. 7: I-V curves of PERKAT under the dark and illumination with AM 1.5 global radiation and 100mW/cm^2 light power.

The device exhibited 0.22 mA/cm^2 short circuit current (Isc) and 0.55V open circuit voltage (Voc) with 0.32 fill factor (FF) which yields in % 0.038 power conversion efficiency (η). In order to improve device efficiency by increasing crystallinity of P3HT and PDI the device was annealed at 100 °C for 15 minutes under inert nitrogen (N_2) atmosphere. After the heat treatment of the device, photovoltaic performance measured again under the same conditions. Post treated device yielded twice of the power conversion efficiency of %0.081 with 0.42 mA/cm short circuit current and 0.55V open circuit voltage with 0.35 fill factor. Enhancement of the efficiency was attributed to enhanced exciton diffusion length by the crystallization of the P3HT and PERKAT in the film and phase separation formation [32]. The photovoltaic parameters investigated under standard conditions were summarized in Table 3.

Table-3

Incident photon to current conversion efficiency (IPCE) spectrum of the OSC based on PERKAT:P3HT (2:1) bulkheterojunction active layer was shown in Fig. 8. The device shows maximum 3.1 % IPCE at 500 nm. The IPCE spectrum shows similarity with PDI absorption spectrum which indicates that the charge injection of the PERKAT is dominant in the D-A blend layer.

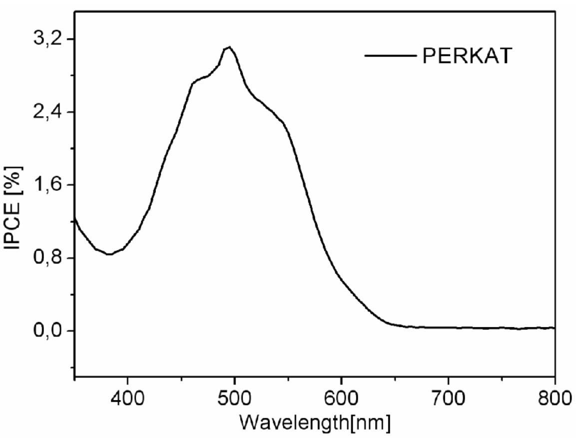

Fig. 8: Incident photon to current conversion efficiency (IPCE) spectrum of the OSC based on PERKAT:P3HT (2:1) bulkhetero-junction active layer.

Photovoltaic performance of the photovoltaic device fabricated with the structure of ITO/ PEDOT:PSS/PERKAT:P3HT (2:1)/LiF/Al is relatively poor in comparison with other "swallow-tail" derivative of PDI [33]. The low photovoltaic conversion efficiency of the device can be attributed to poor interaction of PERKAT and P3HT due to polar poly ethoxy chains and apolar hexyl chains. Poor interaction in the between donor and acceptor molecules causes phase separation and low charge collection efficiency.

Experimental

Perylene-3,4,9,10-tetracarboxylic dianhydride and regioregular poly(3-hexylthiophene) (P3HT) were purchased from Aldrich. 4-nitrocathecol, triethylene glycol monomethyl ether, hydrazine monohydrate, n-butanol and Pd-C were received from Aldrich Company. Imidazole was from Fluka. However, all the solvents (chloroform, toluene, benzonitrile, tetrahydrofuran, and methanol) used in spectroscopic studies were of spectrophotometric grade and used as received. All the other chemicals (hydrochloric acid, sodium carbonate) were purchased from domestic chemical suppliers. Tetrabutylammonium hexafluorophosphate, potassium carbonate, dimethyl formamide, thionyl chloride, benzene, and pyridine were obtained from Merck.

^{1}H spectra were measured on a 400 MHz Bruker spectrometer. The FT-IR spectra were determined on a Perkin-Elmer model Spectrum BX spectrophotometer by dispersing samples in KBr disks. UV-Vis spectra were recorded by Analytic Jena Speedcord S-600 diod-array spectrophotometer and emission spectra measurements were taken on a PTI QM1 fluorescence spectrophotometer. The thermal property of the synthesized PERKAT was measured on a Perkin-Elmer Thermogravimetric Analyzer Pyris 6 TGA instrument under nitrogen atmosphere. The sample was held for 1 min at an initial temperature of 50 $^{\circ}$C and, then heated to 1000 $^{\circ}$C. The heating rate was 20 $^{\circ}$C/min.

Fluorescence quantum yields of the synthesized perylene diimide in different organic solvents were determined with respect to perylene-3,4,9,10-tetracarboxylic-bis-N,N′-dodecyldiimide (N-DODEPER) (Φ_F = 1.0 in chloroform), which was synthesized before, at an excitation wavelength of 485 nm [21]. All the experiments were carried out at 25 ^{o}C, and the compound was analyzed at an optical density below 0.1 to prevent self quenching. Fluorescence emission quenching of P3HT used as donor was observed versus increasing PERKAT concentration. Each addition of 30 μL of PERKAT solution to polymer solution in chloroform was recorded and fluorescence quenching rate constant was calculated by using Stern–Volmer plots.

Synthesis of 1-Chloro-2-[2-(2-methoxyethoxyethoxy] ethane ***(1)***

A mixture of trietylene glycol monomethyl ether (0.52 mmol), toluene (250 mL) and pyridine (45.3 mL) was heated. At reflux temperature, thionyl chloride (0.52 moL) was added drop wise from a dropping funnel under continuous stirring in 3 hours. The mixture was refluxed for an additional 16 hours and then allowed to cool. HCl (0.3 M, 20 mL) solution was added to the mixture at room temperature in 15 min. Then upper organic layer was removed. The product was obtained as light yellow oil. Yield: 70%. ^{1}H NMR ($CDCl_3$; δ, ppm): 3.55-3.51 (t, 2H, –CH_2–Cl), 3.48-3.40(m, 8H,–$CH_2OCH_2CH_2OCH_2$–), 3.34-3.31 (t, 2H,–CH_2OCH_3), 3.16 (s, 3H, –O–CH_3); $C_7H_{15}O_3Cl$.

Synthesis of 1,2-di{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-4-nitrobenzene **(2)**

Chloro-2-[2-(2-methoxyethoxy)ethoxy]ethane (2.8 mmol) was added to a mixture of 4-nitrocathechol (6.4 mmol) and K_2CO_3 (12.8 mmol) in DMF (20 mL) under Ar atmosphere. The mixture was heated at 140 ^{o}C for 19 hours with continuous stirring and finally refluxed for 2 hours. The resulting solution was concentrated. Crude product was purified by column chromatography (neutral alumina, CH_2Cl_2: MeOH, 10:0.4). The compound was obtained as yellow liquid. Yield: 85%. ^{1}H NMR ($CDCl_3$; δ, ppm): 7.8-6.9 (m, 3H, Ar-*H*), 4.2-4.1 (q, 4H, ArOCH_2–), 3.88-3,85 (m, 4H, ArOCH$_2$CH_2–), 3.72-3,69 (m, 4H, –OCH_2CH$_2$OCH$_3$), 3.64-3,58 (m, 8H, –OCH_2CH_2O–), 3.51-3,48 (m, 4H, –CH$_2$CH_2OCH$_3$), 3.33 (s, 6H, –OCH_3); $C_{20}H_{33}NO_{10}$.

Synthesis of 3,4-di{2-[2-(2-methoxyethoxy)ethoxy] ethoxy}aniline **(3)**

Solution of 1-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}-4-nitrobenzene (3 mmol) in n-BuOH (20 mL) was stirred under Ar atmosphere. Pd-C (17 mg of 10%) catalyst was then added. While the mixture was warmed in water bath, hydrazine monohydrate (15 mL) was slowly added from a dropping funnel in 1 hour. The mixture was refluxed for 24 hours and then stirred at room temperature for an additional 24 hours under Ar atmosphere. The mixture was filtered to remove Pd-C and the solvent was removed under vacuum. The residue was purified by column chromatography (neutral alumina, $CHCl_3$: MeOH, 10:0.4). The compound was obtained as yellow liquid. Yield: 90%. ^{1}H NMR ($CDCl_3$; δ, ppm): 7.2-6.13 (m, 3H, Ar-*H*), 4.06-4.01 (q, 4H, ArOCH_2–), 3.78-3,74 (m, 4H, ArOCH$_2$CH_2–), 3.67-3,61 (m, 4H, –OCH_2CH$_2$OCH$_3$), 3.56-3,55 (m, 8H, –OCH_2CH_2O–), 3.33 (m, 4H, –CH$_2$CH_2OCH$_3$), 3.50 (s, 6H, –OCH_3), 3.1-3.06 (s,2H,NH_2) $C_{20}H_{35}NO_8$.

Synthesis of N,N'-Bis(4-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl)-3,4:9,10-perylene tetracarboxydiimide (PERKAT)

Synthetic procedure was done according to literature [22]. Perylene-3,4:9,10-tetracarboxylic dianhydride (0.69mmol), 1 3,4-di{2-[2-(2-methoxyethoxy)ethoxy] ethoxy}aniline (5 mmol) and imidazole (5 g) were heated at 140°C for 4.5 h under Ar atmosphere. Then HCl (200 mL 2N) was added to the reaction solution and the resulting mixture was stirred for 1 h at room temperature then extracted with $CHCl_3$. The organic phase evaporated under vacuum and crude product was purified by column chromatography (CH_2Cl_2: MeOH, 10:1).

FT–IR (cm^{-1}): 2922, 2867, 1704 and 1663 (imide group), 1595, 1512, 1455, 1404, 1361, 1299, 1255, 1178, 1124. ^{1}H NMR ($CDCl_3$; δ, ppm): 8.68-8.59 (q, 8H, ArH (perylene)), 7.20-7.02 (6H, ArH), 4.15 (8H, ArOCH$_2$–), 3.84 (8H, ArOCH$_2$CH$_2$–), 3.7 (8H, –OCH$_2$–CH$_2$OCH$_3$), 3.63-3.61 (16H, –OCH$_2$CH$_2$O–), 3.5 (8H, –CH$_2$OCH$_3$), 3.33 (12H, –OCH$_3$), $C_{64}H_{74}N_2O_{20}$.

Electrochemistry and Spectroelectrochemistry Studies

The electrochemical properties of PERKAT were investigated by Cyclic Voltammetry (CV). CV measurements were recorded by using a CH 660B model Potentiostate from CH Instruments in three-electrode cell. The working glassy carbon electrode was used as working electrode (WE) that was polished before experiment. A platinum wire was used as a counter electrode. A silver wire served as quasi-reference electrode. Measurements were carried out in the 0.1 M $TBAPF_6$ as supporting electrolyte in acetonitrile. The solution in the cell was purged with argon before measurements. Sweep rate was kept constant at 0.1V/s. The oxidation potential of Ferrocene/ Ferrocenium couple at about +0.45V was used as an internal reference.

Photovoltaic Device Fabrication and Characterization

Photovoltaic device was fabricated on indium tin oxide (ITO) covered glass substrates with the structure of ITO/ PEDOT:PSS/Active layer/LiF/Al. First, ITO electrodes were cleaned with detergent, deionized water, acetone and isopropanol and than dried with nitrogen steam. An approximately 100 nm thick layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT: PSS) was spin-coated from aqueous solution (Clevios P AI 4083, H.C. Starck). On top of the PEDOT:PSS, the active layer (80 nm) was spin-coated from chlorobenzene solution (~ 1% wt.) of PERKAT:P3HT (2:1) blend. The top electrode consists of a 0.6 nm thick layer of lithium fluoride (LiF) followed by a 60 nm thick layer of aluminum (Al) deposited by thermal evaporation under $1x10^{-6}$ mbar vacuum. Layer thicknesses were measured by Ambios Tech XP-1 High Resolution profilometer. The active area of cell was 0.16 cm^2. The cell was characterized by measurement of incident photon to current conversion efficiency (IPCE) and Current-Voltage (I-V) characteristics under 100 mW/cm^2 AM 1.5 global irradiation. The fabrication and characterization process were carried out under inert gas atmosphere in the glove box equipped with AM 1.5 solar simulator.

Conclusion

We successfully prepared and characterized new symmetric perylene derivative containing polyoxyethylene chain. Introduction of polyoxyethylene chain to perylene core enhanced its solubility in common organic solvents and increased film-forming capacity. Also, we have studied the optical and electrochemical properties of the dye to evaluate the photovoltaic performance. PERKAT dye exhibited high solubility in common organic solvents. The fluorescence quantum yield (Φ_f) is very low compared to other perylene diimide dyes.

The low photovoltaic conversion efficiency of the photovoltaic device attributed to poor charge transfer formation between PERKAT and P3HT due to phase separation and low charge separation efficiency. Further improvement in the morphology of the bulk heterojunction needed to perform to enhance the photovoltaic conversion efficiency of the device.

References

1. B. Liang, Y. Zhang, Y. Wang, W. Xu and X. Li, J. Mol. Struct. **917**, 133 (2009).
2. Y. Chen, Y. Kong, Y. Wang, P. Ma, M. Bao and X. Li, J. Coll. and Int. Sci. **330**, 421 (2009) .
3. L. Yang, M. Shi, M. Wang and H. Chen, Tetrahedron **64**, 5404 (2008).
4. P. Gawrys, D. Boudinet, M. Zagorska, D. Djurado, J.M. Verilhac, G. Horowitz, J. Pecaud, S. Pouget and A. Pron, Synt. Met. **159**, 1478 (2009).
5. R. Motoyoshi, A. Suzuki, K. Kikuchi and T. Oku, Synt. Met. **159**, 1345 (2009) .
6. H. Dincalp, N. Avcıbası and S. Icli, J. Photochem. and Photobiolog. A: Chem. **185**, 1 (2007).
7. J. Y. Mayorova, P. A. Troshin, A.S. Peregudov, S. M. Peregudova, M. G. Kaplunova and R. N. Lyubovskaya, Commun. **17**, 156 **(**2007).
8. A. H. Qureshi, N. Hussain, S. K. Durrani, H. Waqas, M. Arshad, *Journal of the Chemical Society of Pakistan*, **32**, 761 (2010).
9. Inam-ul-Haque, M. Tariq, *Journal of the Chemical Society of Pakistan*, **32**, 396 (2010).
10. Inam-ul-Haque; H. Saba Hina, *Journal of the Chemical Society of Pakistan*, **32**, 599 (2010).
11. M. Kus, Ö. Hakli, C. Zafer, C. Varlikli, S. Demic, S. Özçelik and S. Icli, Org. Elect. **9**, 757 (2008).
12. X. Zhang, Y. Wu, J. Li, F.Li and M. Li, Dyes Pigments **76**, 810 (2008).
13. L. Fan, Y. Xu and H. Tian, Tetrahed. Lett. **46**, 4443 (2005).
14. J. Fortage, M. S´everac, C. Houarner-Rassin, Y. Pellegrin, E. Blart and F. Odobel, J. Photochem. and Photobiolog A: Chem. **197**, 153 (2008).
15. H.Langhals and F.Sübmeier, J.Prakt.Chem. **341**, 309 (1999).
16. R. A. Cornier and B. A. Gregg, J.Phys.Chem.B. **101**, 11004 (1997).
17. H. Chena, M. Shia, T. Aernoutsb, M. Wanga, G. Borghsb and P. Heremans, Solar Energy Mat. Solar Cells **87**, 521 (2005).
18. S. Ferrere and B. A. Gregg, J.Chem. **26**, 1155 (2002).
19. S. M. Mackinnon and Z. Y. Wang, J. Pol. Sci: A Pol. Chem. **38**, 3467(2000).
20. G. Turkmen, S. Erten-Ela and S. Icli, Dyes Pigments **83**, 297 (2009).
21. S. Icli and H. Icil, Spect. Lett. **29(7),** 1253 (1996).
22. H. Langhals, R.Ismael and O. Yuruk, Tetrahedron 56, **5435** (2000).
23. S. Asır, A. S. Demir and H. Icil, Dyes Pigments **84**, 1 (2010) .
24. E. M. Ebeid and S. A. El-Daly, J.Phys.Chem. **92**, 4565 (1988).
25. K. Balakrishnan, A. Datar, T. Naddo, J. Huang, R.Oitker, M. Yen, J. Zhao and L. Zang, J. Am. Chem.Soc. **128,** 7390 (2006).
26. JC. Scaino, CRC Handbook of Organic Photochemistry, Vol II. Florida, CRC Pres**, (**1989).
27. J. B. Bodapati and H. Icil, Dyes Pigments **79,** 224 (2008).
28. M. W.Holman, P.Yan, D. M. Adams, S. Westenhoff and C. Silva, J.Phys.Chem. A **109**, 8548 (2005).
29. JD. Coyle, Introduction to organic photochemistry. Great Britain: John WileySons Ltd; (1989).
30. JC.Scaino, CRC Handbook of Organic Photochemistry, Vol II. Florida, CRC Pres, (1989).
31. SK. Lee, Y. Zu, A. Herrmann, Y. Geerts, K. Mullen and AJ. Bard, Journal of the American Chemical Society, **12**, 3513 (1999).
32. J. J. Dittmer, E. A. Marseglia and R. H. Friend, Adv. Mat. **12**, 1270 (2000).
33. A. Liscio, G.D. Luca, F. Nolde, V. Palermo, K. Müllen and P. Samori, *Journal of the American Chemical Society,***130**,780 (2008).