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A Neutral Stable and Soluble Polymer Radical with Low Band Gap and Its Photovoltaic Application

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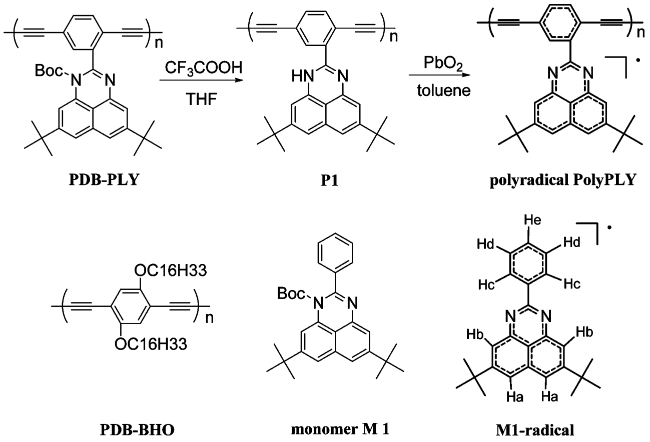
Because of their possible intrinsic electrical[1,2] and magnetic properties,[3] stable neutral organic[4,5] and polymer radical[6,7] materials have been sought for many prospective plastic device applications, including electronic, optoelectronic, magnetoelectronic devices and even integrated systems with multifunctionality.[5,8,9] Recent examples for these neutral stable radicals include the small ring systems with N and S atoms,[10,11] phenalenyl,[12,13] spiro-conjugated phenalenyl,[2,5] triphenylmethyl systems,[4,14] polyradicals with pendant phenoxyl and nitroxide radical unit,[7] and the two-dimensionally dendritic macrocyclic poly(1,3-phenylenephenylmethine)s polyradical.[6]

For high performance polymer-based bulk-heterojunction (BHJ) photovoltaic (PV) cells, several very important material intrinsic factors were identified recently, including the donor's band gap, the lowest unoccupied molecular orbital (LUMO) level and the charge carrier mobility.[15] Thereby, semiconducting polymers with a band gap of ∼1.5 eV, LUMO level of ∼3.8 eV, and high charge mobility have been sought for optimized plastic solar cell applications.[15] The intrinsic relatively small band gap due to the singly occupied molecular orbital (SOMO) and larger conducting bandwidth[2] prompts us to expect that these neutral stable radical materials, particularly the stable semiconducting polymer neutral radicals, might offer optimized solar light absorption and more efficient charge transportation channel toward optimized overall solar cell performance.[16] Taking advantages of these intrinsic properties of neutral stable polymer radicals[2,5,6,12] and the large linear conjugation of poly(*p*-diethynylbenzene)s (PDBs), we now report the synthesis of the first neutral stable and soluble polymer radical with pendant conjugated phenalenyl radical unit and its initial PV application result.

The stable polyradical PolyPLY (Scheme 1) was synthesized in seven steps from 2,5-dibromo-benzaldehyde, and the synthesis is described in detail in the Supporting Information. Briefly, the poly(*tert*-butyl-5,8-di-*tert*-butyl-2- diethynylbenzene-1*H*-perimidine-1-carboxylate) (PDB−PLY) was synthesized through a palladium-catalyzed oxidative homocoupling with diisopropylamine as the base to produce diyne linkage. The obtained polymer was then deprotected by CF$_3$COOH to give the polyradical precursor poly(5,8-di-*tert*-butyl-2-diethynylbenzene-1*H*-perimidine) (P1). The structure of P1 was confirmed by ^{1}H NMR, GPC and MALDI−TOF (see SI). Oxidization of P1 using PbO$_2$ in toluene stirring overnight and depositing by pouring the solution into methanol gave the targeted polyradical PolyPLY, which has a rather good solubility in common organic solvents, such as CHCl$_3$, THF, and toluene. The molecular weight of its precursor P1 and the polyradical PolyPLY measured by GPC were $M_n = 7.8 \times 10^3$ and 8.5×10^3 g mol^{-1} respectively, which were calibrated relative to polystyrene standards. The corresponding polymerization degree is about 19−21 and polydispersity index (PDI) is 1.5 and 1.7, respectively.

Scheme 1. Synthesis of Polyradical PolyPLY



To estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, we examined the electrochemical property of polyradical PolyPLY by cyclic voltammetry (CV) spectrometry, which gave an irreversible oxidation and reduction process at a sweep rate of 100 mV s^{-1} in the MeCN solution with tetrabutylammonium perchlorate (TBAPF$_6$) as the electrolyte (Figure 1, left). The onsets of oxidation and reduction peaks were at +0.29 and −1.34 V respectively vs Ag/Ag$^+$ (see the onsets shown in Figure 1). On the basis of the onsets, the values for HOMO and LUMO were calculated to be −5.01 and −3.38 eV. The band gap derived from the difference between oxidation and reduction potentials of PolyPLY was estimated to be 1.63 eV.

The solution absorption spectra of the model monomer M1, M1-radical, model polymer PDB−BHO, PDB−PLY, and polyradical PolyPLY in chloroform solution are shown in Figure 1 (right). The large bathochromical shift (136 nm) of absorption maximum of PDB−PLY ($\lambda_{max} = 533$ nm) compared with that of the monomer M1 ($\lambda_{max} = 397$ nm) suggests an extended π-conjugation arising along the backbone. Interestingly, the absorption maximum position of PDB−PLY shifted even to a longer wavelength comparing with that (442 nm) of model polymer PDB−BHO (Scheme 1) which had the same backbone but without π-conjugation contributation due to the alkyl arm.[17] The alkyl chain on this model polymer was used to obtain the desired solubility. This indicates that there is significant π-conjugation delocalization between the planar π-conjugated 1,3-diazaphenalenyl (PLY) skeleton with the main chain for our polymers of PDB−PLY and the polyradical PolyPLY. The UV−vis spectrum of PolyPLY solution exhibits a red shift (ca. 8 nm) of λ_{max} and a new peak around 700 nm arose compared

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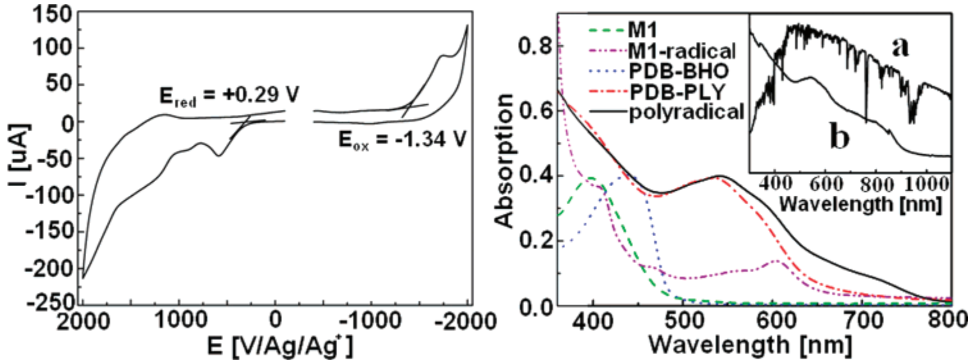

Figure 1. Left: Cyclic voltammogram of polyradical film on Pt/C electrode at 100 mV s^{-1} in 0.01 M tetrabutylammonium perchlorate/MeCN. The onsets of oxidation and reduction peaks were at +0.29 V and −1.34 V respectively vs Ag/Ag$^+$. Right: UV−vis absorption spectra of model monomer M1, M1-radical, model polymer PDB−BHO, PDB−PLY and polyradical PolyPLY in CHCl$_3$ solution. Inset: (a) solar simulator spectrum (AM 1.5) and (b) UV−vis absorption spectra of the PolyPLY film.

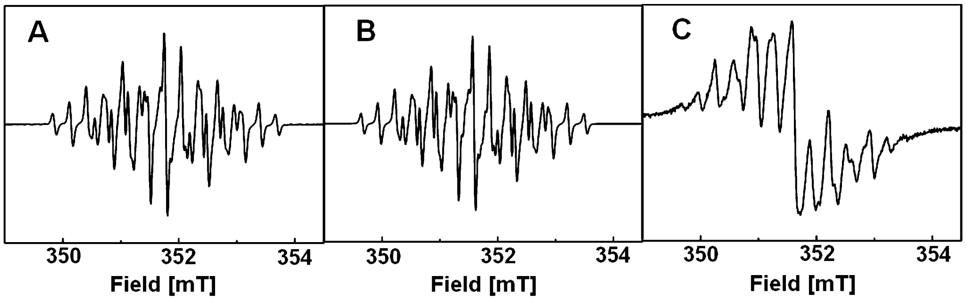

Figure 2. Hyperfine ESR spectra of (A) observed M1-radical (1 mM), (B) simulated for M1-radical, and (C) the observed PolyPLY (5 mM of the repeating unit concentration) in toluene at room temperature.

with that of its precursor PDB−PLY, which expands up to ~750 nm (black solid line in Figure 1). If the UV−vis spectrum of the monomer radical M1-radical is compared with that of precursor M1, a new peak around 600 nm appears. Considering the likely bathochromical shift due to the conjugation along the backbone, the peak of PolyPLY around 700 nm was assigned to be the polymer radical. The derived band gap of this polyradical from the energy absorption edge of the spectrum is 1.59 eV, in agreement with that obtained from CV measurement. Because of the tailing of the absorption toward longer wavelength, the exact position of the optical band gap was found to be difficult to be established, and the actual value may be lower than what we conservatively estimated. In addition, the film optical spectrum of PolyPLY remains practically identical to its solution spectrum without any bathochromic shift which is commonly observed for many π-conjugated polymers, indicating that no additional π-stacking interaction appearing when going from solution to film, which may be due to the steric hindrance effect of bulky side chain. The long tailing around 700 nm can be observed both in solution and film absorption spectrum, which indicated that it was intrinsic characteristic but not a reflection on poor film quality. From the inset in Figure 1, we can also see that the absorption spectrum of PolyPLY in the range 450−800 nm matches relatively well with the solar spectrum (AM 1.5).

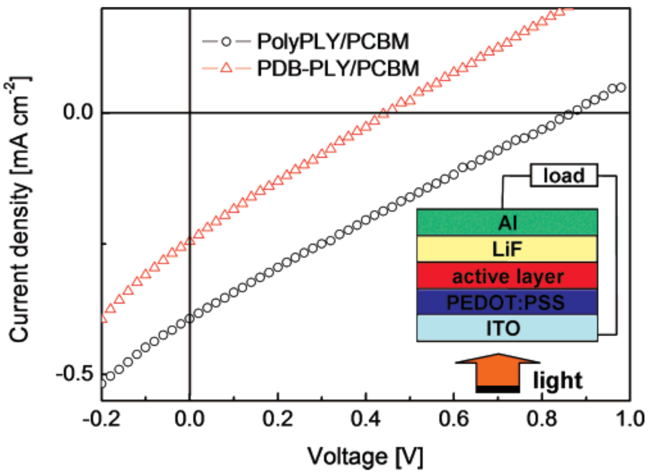

Figure 3. Current density vs voltage ($J-V$) characteristics of ITO/PEDOT:PSS/PolyPLY:PCBM/LiF/Al and ITO/PEDOT:PSS/PDB−PLY:PCBM/LiF/Al devices under white-light illumination (AM 1.5 conditions). The inset shows the device configuration used.

The polyradical PolyPLY and monomer radical M1-radical were characterized with ESR spectrum in toluene as shown in Figure 2. The spin density distribution over the 1,3-diazaphenalenyl unit in M1-radical and PolyPLY was supported by the clear hyperfine structure. In addition, the density functional theory calculations for M1-radical based on the DFT calculation by using Gaussian 03 at the UB3LYP/EPR-II level of theory (see Figure S5 in SI) was carried out, showing a weak delocalized π-spin densities exist on the substituted benzene ring. M1-radical gave a g value of 2.0033 and the hyperfine coupling constants (mT) were estimated by spectral simulation which referring to the calculation data: $a_{\mathrm{Ha}} = -0.720$, $a_{\mathrm{Hb}} = -0.631$, $a_{\mathrm{H}t\text{-}\mathrm{Bu}} = 0.011$, $a_{\mathrm{N}} = 0.283$, $a_{\mathrm{Hc}} = 0.020$, $a_{\mathrm{Hd}} = -0.007$, and $a_{\mathrm{He}} = 0.018$. The values of the g and hyperfine coupling constants for this model radial are consistent with other similar phenalenyl radicals.[13,18] The polyradical PolyPLY gave a rather similar ESR with $g = 2.0031$, and some fine structure has disappeared with the peaks widened comparing with that of the monomer radical. The PolyPLY is rather stable in solid state and the ESR of its solid sample does not show any significant change under air for months at room temperature.

With the low band gap and well solar light absorption of PolyPLY, we fabricated PV cells using this polymer radical. The $J-V$ characteristic plot (Figure 3) of the device based on the PolyPLY/PCBM blend (1:0.6) under illumination (AM 1.5, 50 mW cm^{-2}) exhibits a short circuit current density (J_{sc}) of 0.39 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.86 V, a fill factor (FF) of 0.24 and the energy conversion efficiency $\eta =$ 0.17%. As a comparison, the device using PDB−PLY/PCBM blend as the active layer, where no-radical polymer PDB−PLY replaces polyradical PolyPLY, shows the $J_{sc} = 0.25$ mA cm^{-2}, $V_{oc} = 0.44$ V, $FF = 0.24$, and $\eta = 0.053\%$. The energy efficiency improvement of PolyPLY radical device could come from several reasons, and we argue that the presence of the unpaired electrons may increase the carrier concentration,[19] which is crucial to determine the short circuit current.[20] In addition, the improvement of the hole extraction of the device may lead to the shift of its quasi Fermi level, resulting in an increase in the V_{oc}.[21] As the first example of applying neutral stable polyradicals in the PV device, the initial power conversion efficiency of which was not prominent, but further optimization in the materials and devices are expected to have better PV performance.

In summary, we synthesized the first neutral stable polyradical with π-conjugated phenalenyl radical unit. This polyradical has a low band gap value of 1.59 eV and its application for PV device has been studied. This polyradical exhibits a rather good solubility in common organic solvents and stability in air. The conjugation between the side chain of 1,3-diazaphenalenyl unit and poly(p-diethynylbenzene)s backbone causes a substantial lowering of the band gap relative to other poly(p-diethynylbenzene)s.[17] Initial studies have showed that the PV device with radicals doped has improved the conversion efficiency.[21] Studies are underway for a more comprehensive investigation about its transport and magnetic properties and solar cell applications.

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Supporting Information Available: Text giving the preparation of the monomers and polymers, PV fabrication and measurement, a scheme showing the syntheseis process, and a figure showing the MALDI mass spectrometry of P1, figures showing GPC data for polymers, and a figure showing spin density calculation results using Gaussian 03 for M1-radical. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Haddon, R. C. *Nature (London)* **1975**, *256*, 394−396.
(2) Pal, S. K.; Itkis, M. E.; Tham, F. S.; Reed, R. W.; Oakley, R. T.; Haddon, R. C. *Science* **2005**, *309*, 281−284.
(3) Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893.
(4) Hicks, R. G. *Org. Biomol. Chem.* **2007**, *5*, 1321−1338.
(5) (a) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. *Science* **2002**, *296*, 1443−1445. (b) Mandai, S. K.; Samanta, S.; Itkis, M. E.; Jensen, D. W.; Reed, R. W.; Oakley, R. T.; Tham, F. S.; Donnadieu, B.; Haddon, R. C. *J. Am. Chem. Soc.* **2006**, *128*, 1982−1994.
(6) (a) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *Science* **2001**, *294*, 1503−1505. (b) Rajca, A.; Rajca, S.; Wongsriratanakul, J. *J. Am. Chem. Soc.* **1999**, *121*, 6308−6309.
(7) (a) Nishide, H.; Hozumi, Y.; Nii, T.; Tsuchida, E. *Macromolecules* **1997**, *30*, 3986−3991. (b) Miyasaka, M.; Yamazaki, T.; Tsuchida, E.; Nishde, H. *Macromolecules* **2000**, *33*, 8211−8217. (c) Nishide, H.; Ozawa, T.; Miyasaka, M.; Tsuchida, E. *J. Am. Chem. Soc.* **2001**, *123*, 5942−5946. (d) Kaneko, t.; Makino, T.; Miyaji, H.; Teraguchi, M.; Aoki, T.; Miyasaka, M.; Nishide, H. *J. Am. Chem. Soc.* **2003**, *125*, 3554−3557. (e) Suga, T.; Pu, Y. J.; Kasatori, S.; Nishide, H. *Macromolecules* **2007**, *40*, 3167−3173.
(8) Das Sarma, S. *Am. Sci.* **2001**, *89*, 516−523.
(9) Wolf, S. A.; Awschalom, D. D.; Buhrman, R. A.; Daughton, J. M.; von Molnar, S.; Roukes, M. L.; Chtchelkanova, A. Y.; Treger, D. M. *Science* **2001**, *294*, 1488−1495.
(10) Rawson, J. M.; Alberola, A.; Whalley, A. *J. Mater. Chem.* **2006**, *16*, 2560−2575.
(11) Cordes, A. W.; Haddon, R. C.; Oakley, R. T. *Phosphorus Sulfur Silicon Relat. Elem.* **2004**, *179*, 673−684.
(12) Koutentis, P. A.; Chen, Y.; Cao, Y.; Best, T. P.; Itkis, M. E.; Beer, L.; Oakley, R. T.; Cordes, A. W.; Brock, C. P.; Haddon, R. C. *J. Am. Chem. Soc.* **2001**, *123*, 3864−3871.
(13) Morita, Y.; Aoki, T.; Fukui, K.; Nakazawa, S.; Tamaki, K.; Suzuki, S.; Fuyuhiro, A.; Yamamoto, K.; Sato, K.; Shiomi, D.; Naito, A.; Takui, T.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1793−1796.
(14) Rajca, A.; Shiraishi, K.; Vale, M.; Han, H. X.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 9014−9020.
(15) Scharber, M. C.; Wuhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. L. *Adv. Mater.* **2006**, *18*, 789−794.
(16) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953−1010.
(17) Shi, C. J.; Yang, K. X.; Cao, Y. *Synth. Met.* **2005**, *154*, 121−124.
(18) Goto, K.; Kubo, T.; Yamamoto, K.; Nakasuji, K.; Sato, K.; Shiomi, D.; Takui, T.; Kubota, M.; Kobayashi, T.; Yakusi, K.; Ouyang, J. Y. *J. Am. Chem. Soc.* **1999**, *121*, 1619−1620.
(19) Yamamori, A.; Adachi, C.; Koyama, T.; Taniguchi, Y. *Appl. Phys. Lett.* **1998**, *72*, 2147−2149.
(20) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324−1338.
(21) Vaddiraju, S. *Chem. Mater.* **2007**, *19*, 4049−4055.

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