Macromolecules

Dicyano-Substituted Poly(phenylenevinylene) (DiCN-PPV) and the Effect of Cyano Substitution on Photochemical Stability

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ABSTRACT: A didecyloxy-substituted poly(phenylenedicyanovinylene), DiCN-PPV, has been synthesized. The dicyano-substituted vinylene units exist in both *trans* and *cis* (~65:35) conformations as determined by ¹H NMR analysis, and cannot be converted to all *trans* due to the presence of a thermodynamic equilibrium of the two conformations, in contrast to the vinylene units in regular PPVs. The unusually high *cis* content makes this polymer highly amorphous, very soluble in organic solvent, and highly fluorescent in the solid state with an estimated quantum yield up to 0.34, four times more fluorescent than its chloroform solution. The LUMO and HOMO energies of the new polymer were measured by cyclovoltammetry. The cyano groups in DiCN-PPV brings a decrease in LUMO energy by



0.79 eV, and makes the polymer more stable to intense white light (>20 times as strong as the sunlight) than poly(2,5-didecyloxy-1,4-phenylenevinylene), $C_{10}O$ -PPV, by more than 2 orders of magnitude. The excellent photochemical stability and high fluorescence quantum yield in the solid state make DiCN-PPV a good candidate for outdoor fluorescent applications such as remote optical sensing.

1. INTRODUCTION

Fluorescent conjugated polymers have many applications such as light emitting,¹⁻³ solid-state dye lasing,^{4,5} biological imaging and sensing,⁶⁻¹⁰ and chemical sensing.¹¹⁻¹⁵ Fluorescent materials can also be incorporated into microparticle taggants for military applications such as remote and covert detection of friend or enemy targets, supporting new capabilities in covert search and rescue (downed pilots), intelligence gathering (tracking documents, packages), and security measures (detection of breaches and intruders).¹⁶ However, organic materials usually have relatively low photochemical stability,¹⁷ which limit their applications and lifetime. There has been significant effort on developing air-stable organic functional materials for n-type transistor application,¹⁸ but little research on photostable organic fluorescent polymers has been reported.¹⁹

It is well established that oxidation stability of conjugated organic compounds and polymers can be enhanced by lowering HOMO or LUMO energy level of molecules or polymers via modification of conjugated system with electron-withdrawing groups. This strategy has been applied to air-stable n-type organic field-effect transistor (FET) materials.¹⁸ Air stability was observed for electron-deficient oligothiophene derivatives and fused arene imides with LUMO energy lower than a certain level (ranging from -4.1 to -4.8 eV, depending on the molecular structure). When molecular materials are exposed to light, the LUMOs are also populated with electrons (similar to n-type materials after electron injection) and thus their LUMO energy levels should also largely determine their photochemical stability.

Poly(alkoxyphenylenevinylene)s and poly(2,5-dialkoxycyanoterephthalylidene) have been investigated for light emission application.^{20,21} Phenylenevinylene oligomers²² and polymers^{17,23} are known to undergo fast photochemical oxidation by singlet oxygen.²² To systematically study the effect of LUMO energy on photostability of conjugated polymers without the complication by different side chains,¹⁷ we synthesized three polymers (Chart 1) with different number

Chart 1Chemical structures of $C_{10}O$ –PPV, CN–PPV, and DiCN–PPV polymers synthesized and used in photostability study. R = *n*-decyl.



of cyano groups on the exocyclic double bond in PPVs: poly(2,5-didecyloxy-1,4-phenylenevinylene) or $C_{10}O$ –PPV, poly(2,5-didecyloxycyanoterephthalylidene) or CN–PPV, and poly(2,5-didecyloxy-7,8-dicyano-1,4-phenylenevinylene), DiCN–PPV. Introduction of one cyano group on every vinylene unit lowers the LUMO energy by 0.56 eV. An

 Received:
 April 1, 2013

 Revised:
 May 13, 2013

additional cyano group further reduces LUMO energy by 0.41 eV without significantly changing the absorption peak wavelength. Via a comparative study of photostability of films of $C_{10}O$ -, CN- and DiCN-PPVs under white light from a xenon lamp, a dramatic effect of CN substitution on decay rate constant has been observed. It is also found that the presence of a high content of *cis* C=C in the polymer structure has a dramatic effect on the photoluminescence (PL) efficiency in both solution and solid state, and renders the new polymer the only polymer known to us that is much more fluorescent in the solid state than in the solution.

2. EXPERIMENTAL SECTION

NMR data were obtained from a Bruker Avance 300 MHz NMR Spectrometer. Elemental analyses were performed by Atlantic Microlab Inc. Molecular weights of polymers were determined using a Viscotek TriSec GPC system with universal calibration. Polystyrenes were used as the standards and tetrahydrofuran as the solvent. The polymer films were spin-coated from the polymer solutions in odichlorobenzene on glass substrates. UV–vis spectra were obtained from an Agilent 8453 photodiode array UV–vis absorption photospectrometer. Thermal analyses (DSC and TGA) were performed using Perkin-Elmer TGA-6 and DSC-6 systems.

Electrochemical studies were performed on a Bioanalytical (BAS) Epsilon-100w trielectrode cell system with a Pt working electrode, an ancillary Pt electrode, and a silver reference electrode in a CH_3CN solution of 0.01 M AgNO₃ and 0.1 M tetrabutylammonium hexafluorophosphonate. The measurements were performed in a N₂-purged 0.1 M TBA-HFP/acetonitrile solution at a scan rate of 100 mV/s. Ferrocene (2 mM in 0.10 M TBA-HFP/CH₃CN solution) was used as an internal reference standard and its HOMO level of -4.80 eV was used in calculations.

Photoluminescence (PL) was measured on an Edinburgh FS920 fluorescence spectrometer. All measurements were conducted in air without using an inert gas to purge solution or protect films. Correction of PL spectra was carried out using the emission correction file of the spectrometer. The emission correction was performed in the range of 200–900 nm using deuterium-tungsten light source with known spectral distribution. A high power Newport light source (model 66903) equipped with a 300 W xenon light bulb and a Newport power supply (Model 69911) was used for the photostability study. The output from the light source was used without filtering. Light intensity was adjusted through a focus lens and measured by a Newport 70260 power meter with a 3A-P-SH-V1 thermal head. The aperture diameter of the power meter is 1.2 cm and the unit intensity is calculated to be 2200–2600 mM/cm², about 22–26 times of standard one sun intensity.

2,5-Bis(bromocyanomethyl)-1,4-bis(decyloxy)benzene (2). A literature producedure²⁵ for bromination of phenylacetonitrile was followed with minor modifications. A solution of 2,5-bis-(cyanomethyl)-1,4-bisdecyloxy-benzene (1²¹) 0.905 g, 1.93 mmol), benzoyl peroxide (33.0 mg, 0.135 mmol), tetrachlorocarbon (5.7 g), and N-bromosuccinimide (NBS, 0.704 g, 3.96 mmol) was heated in a closed bottle in a 85 °C oil bath for 3 h. After removing succinimide by filtration, the residue was purified using a silica gel (200 mL) column and 1:40 EtOAc/hexanes as the eluent. 320 mg of yellow solid was obtained after crystallization from hexanes. Yield: 38.8%. The main reason for the low yield is decomposition of the product in the column into a yellow colored species. ¹H NMR (CDCl₃) of 2: δ (ppm) 0.89 (t, 4H, J = 6 Hz, 1.1-1.7 (m, 28H), 1.85 (m, J = 6.4 Hz), 4.09 (t, 4H, J = 6.4 Hz)5.1 Hz), 5.86 (s, 2H), 7.20 (s, 2H). ¹³C NMR (CDCl₃) of **2**: δ (ppm) 149.57, 124.75, 116.22, 112.40, 69.46, 29.54 (two carbon peaks overlapped), 29.33, 29.30, 29.06, 26.02, 22.69, 21.83 (CHBrCN), 14.14. Anal. Calcd: C, 57.51; H, 7.40; Br, 25.51; Found: C, 57.70; H, 7.53; Br, 25.47.

2-Bromomethyl-1,4-bis(decyloxy)benzene (4). A mixture of 1,4-bis(decyloxy)benzene (3, 78.12 g, 0.2 mol), paraformaldehyde (7.207g, 0.24 mol), glacial acetic acid (230 g), and 30 wt % HBr/

HOAc (110 mL) was stirred at 60 °C for 3 h. The resulting mixture was diluted with water (300 mL), and then kept in a freezer for 1 h. The solid products were collected by filtration, and then dissolved in hexanes. The hexane solution was washed with water (50 mL), aqueous NaHCO₃ (10 mL), dried over MgSO₄, and condensed by rotary evaporation. The crude product had a composition of ~15% of 1,4-bisdecyloxybenzene, ~20% of 1, and ~65% of 4 by ¹H NMR analysis. Separation of 1 and 4 was not practical using silica gel chromatography. The crude product was used in the next step without purification. ¹H NMR (CDCl₃) of 4: δ (ppm) 0.88 (t, *J* = 6.8 Hz, 6H), 1.1–1.6 (m, 28H), 1.77 (m, 4H), 3.88 (t, *J* = 6.6 Hz, 2H), 3.95 (t, *J* = 6.4 hz, 2H), 4.52 (s, 2H), 6.78 (m, 2H), 6.89 (d, *J* = 2.4 Hz, 1H). The chemical shift of CH₂Br is same as the literature value for CH₂Br in a similar compound: 2,5-bisbromomethyl-1-methoxy-4-(2-ethylhexyloxy)benzene.²⁶

2-Cyanomethyl-1,4-bis(decyloxy)benzene (5). A mixture of the crude product of 4 (27.42 g), sodium cyanide (5.15 g) and DMSO (130 mL) was stirred at 53 °C for 23 min. The mixture was diluted with water (250 mL), extracted with hexanes (100 mL × 3), dried over MgSO₄ and condensed on a rotary evaporator. The crude product was purified twice by silica gel (1L) column chromatography using 1:40 EtOAc/hexanes as the eluent. The product was further purified by recrystallization from hexanes at -7 °C. Yield: 16.9 g, 59% for the two steps combined. ¹H NMR (CDCl₃) of **5**: δ (ppm) 0.88 (t, *J* = 6.8 Hz, 6H), 1.1–1.6 (m, 28H), 1.76 (m, 4H), 3.67 (s, 2H), 3.92 (m, 4H), 6.78 (s, 2H), 6.94 (s, 1H). ¹³C NMR (CDCl₃) of **5**: δ (ppm) 153.07, 150.30, 119.53, 118.01, 115.97, 114.57, 112.26, 68.74 (two OCH₂ overlapped), 31.93, 29.61, 29.44, 29.36, 26.14, 26.07, 22.71, 18.26 (CH₂CN), 14.13. Anal. Calcd: C, 78.27; H, 11.03. Found: C, 78.25; H, 11.04.

2-Bromo-5-(bromocyanomethyl)-1,4-bis(decyloxy)benzene (6). A mixture of **5** (1.09 g, 2.537 mmol), azobis(isobutyronitrile) (0.15 mol equiv, 62.9 mg), tetrachlorocarbon (11 g), and bromine (0.812 g) was heated in a closed 16 mL-vial in a 100 °C oil bath (with 1/3 of vial above the oil) for 30 min. The reaction was worked up and the crude product was purified in a similar way used for the purification of **6** to afford 556 mg of white solid product. Yield: 35%. ¹H NMR (CDCl₃) of **6**: δ (ppm) 0.88 (t, 4H, *J* = 6 Hz), 1.1–1.7 (m, 28H), 1.83 (m, 4H), 4.07 (m, 4H), 5.82 (s, 1H), 7.10 (s, 1H), 7.15 (s, 1H). ¹³C NMR (CDCl₃) of **6**: δ (ppm) 150.04, 149.66, 121.24, 117.63, 116.37, 115.79, 113.27, 70.25(OCH₂), 69.45 (OCH₂), 31.92, 29.55, 29.34, 29.29, 29.13, 29.08, 26.00, 25.97, 22.70, 22.31 (CHBrCN), 14.13 (only OCH₂ in the two decyl groups are well separated, other pairs are completely overlapped). Anal. Calcd: C, 57.25; H, 7.72; Br, 27.20. Found: C, 57.42; H, 7.78; Br, 27.41.

2,3-Bis(4-bromo-2,5-bis(decyloxy)phenyl)-but-2-enedinitrile (7, the Model Compound). To a solution of 6 (0.585 g, 1.00 mmol) in 2 mL of THF, a solution of t-BuOK (0.97 equiv, 108.8 mg) in THF (1 mL) was added. Then, 5 min after the addition, the ¹H NMR spectrum of the reaction mixture showed ~55% cis and ~45% trans products. THF was removed by rotary evaporation. The residue was worked up using hexane. The hexane solution was washed with water and dried. Crystals formed in concentrated hexane solution and were collected by filtration and washed with MeOH to afford 0.17 g yellow pure trans product. The filtrate was concentrated and passed through a silica gel column to yield 50 mg trans product. No pure cis product was obtained due to *cis* to *trans* isomerization in the column. ¹H NMR (CDCl₃) of trans 7: δ (ppm) 0.87 (m, 12H), 1.2–1.6 (m, 56H), 1.82 (m, 8H), 4.02 (m, 8H), 7.01 (s, 2H), 7.22 (s, 2H). Characteristic ¹H NMR peaks of cis 7 can be easily identified in the spectrum of a product mixture: ¹H NMR (CDCl₃) of *cis* 7: δ (ppm) 3.61 (t, J = 6.5 Hz, 4H), 3.87 (t, J = 6.8 Hz, 4H), 7.43 (s, 2H), 7.07 (s, 2H). The two isomers can be easily identified by ¹H NMR as the aromatic and OCH₂ protons in the *cis* isomer are significantly shifted to the higher field as compared to those in the trans isomer due to the shielding effect of the two cis benzene rings.

Poly(2,5-didecyloxy-7,8-dicyano-1,4-phenylenevinylene), **DiCN–PPV.** To a solution of 2 (0.209 g, 0.333 mmol) and 6 (0.0104 mmol, 5.31 mg) in 2 mL of THF was added a solution of *t*-BuOK (2 equiv, 80.4 mg) in THF (2 mL). The reaction was continued for 10 Scheme 1. Synthesis of DiCN-PPV and a Model Compound 7



Figure 1. ¹H NMR spectrum of DiCN-PPV in CDCl₃.

min. The resulting mixture was dropped into MeOH. The yellow polymer solid was collected by filtration, and vacuum-dried. Yield: 0.157 g, 98.4%. Anal. Calcd: C, 76.96; H, 9.50; N, 5.86; Br, 0.82. Found: C, 76.97; H, 9.54; N, 5.60; Br, 0.55. $C_{10}O-PPV^{24}$ and $CN-PPV^{21}$ were synthesized according to the

literature procedures.

3. RESULTS AND DISCUSSION

Synthesis. The synthetic route of DiCN–PPV is shown in Scheme 1, and is different from a literature method used for synthesis of an analogous polymer (with MeO and EHO side chains).²⁷ Compound 1 was brominated to give monomer 2 using a literature procedure with minor modifications.²⁵ 6 was synthesized from 1,4-bisdecyloxybenzene (3) in three steps. The monobromomethylation of 3 was effected using the same procedure as that used for dibromomethylation of 3^{24} except that only 1.2 mol equiv of paraformaldehyde was used. Separation of 4 from the dibromomethylation side product was not performed due to their similar R_f values. Bromination of 5 also happened to the benzene ring and led to the formation of compound **6**.

Compound 2 has not been reported in the literature. But its monofunctional analogues, iodophenylacetonitrile compounds, have been reported and can be converted into 2,3-diphenyl-but-2-enedinitrile compounds in the presence of MeONa.² Applying similar condition to 2 should polymerize it into DiCN-PPV as shown in Scheme 1. Potassium tert-butoxide was used instead of MeONa because NaOMe can lead to the further conversion of the formed dicyanovinylene unit into maleimide.²⁸ The polymerization reaction was instantaneous at room temperature. A small amount of 6 was added as a terminator to control molecular weight (MW). When 1% molar equivalent of 6 was used, the polymer still has a high MW (M_{w}) $M_{\rm p} = 63015/17901$) and was not fully soluble. When 5% molar equivalent of 6 was used, the M_w was reduced to 14 k Da, and the polymer became fully soluble and was used in the following study. The amount of base was controlled to be exactly 1 molar equiv to avoid cross-linking of the formed polymer. The ¹H NMR spectrum is shown in Figure 1. Several peaks are present in the region of 4 ppm for O–CH₂ protons and in the aromatic region for phenyl protons. The peak at 4.15 ppm is assigned to O-CH₂ in *trans* units while the minor peaks in the higher field are assigned to O-CH2 in cis units, similar to situation in $C_{10}O-PPV$ ²⁴ The intensity of this peak accounts for ~65% of the overall intensity of all peaks in the region of 3.5-4.2 ppm. Accordingly, the peak at 7.2 ppm, which accounts for \sim 65% of the integration of the aromatic peaks, can be assigned to the phenyl units next to trans-dicyanovinylene units. It is noticed that this chemical shift (7.2 ppm) is significantly smaller than that (7.78 ppm) of trans-bis(4-methoxyphenyl)fumaronitrile in the literature.²⁸ This difference is due to the presence of 2,5decyloxy groups which forces the benzene ring and the vinyl unit out of plane even in the trans conformation and thus reducing the influence of the electron withdrawing cyano groups.

The presence of the *cis* structures introduce kinks in polymer chains and reduce its conjugation length since the benzene rings cannot be coplanar with the vinylene unit. Cis-to-trans conversion under acidic condition, which was successful for



Figure 2. Left: DSC trace of DiCN-PPV. Middle: TGA analysis of DiCN-PPV. Right: wide-angle XRD results of DiCN-PPV.

 $C_{10} O{-} PPV^{24}$ and SF-PPV, 29 did not produce a significant difference in ¹H NMR spectrum of DiCN-PPV. There could be two different reasons for the failed conversion: (1) The electron-withdrawing cyano groups reduce the electron density of the vinyl to such a low level that the proton can no longer add to the vinylene to form a cationic intermediate, or (2) the two conformations are similar in energy and thus can thermodynamically coexist. To find the true reason, a model compound (7) was made from dimerization of 6 (Scheme 1) to study the *cis/trans* behavior of the dicvanovinylene unit. The product 7 was a mixture of cis/trans dimers. Pure trans isomer was obtained from silica gel column chromatography of the mixture as the cis compound moves slightly slower. Pure cis isomer was not obtained due to its faster isomerization in the column. It was found that *trans-cis* isomerization happened to trans isomer of 7 in CDCl₃ solution (usually contains a trace amount of acid) at ambient temperature after for a few days. After 40 days in the NMR tube, the trans-cis ratio reached an equilibrium value of 2.9:1 (or 74% trans). So, the existence of cis and trans thermodynamic equilibrium prevents the polymer from being converted to all trans.

Solubility, Thermal Properties, and XRD Study. Because of the presence of *cis* structure, which is highly nonplanar, DiCN–PPV is highly soluble in common polar organic solvents such as chloroform, tetrahydrofuran, etc. DSC thermograph (Figure 2, left) of the polymer does not show any significant phase transition or melting peak. The decomposition onset temperature is about 250 °C by DSC. However, the polymer does not lose weight until 354 °C as shown in the TGA result (Figure 2, middle). XRD experiments (wide-angle) were performed on as-cast thick films of DiCN–PPV (Figure 2, right). No higher order peaks were observed other than a zeroth order peak at 3.7° .

Optical Absorption and Electrochemical Properties. The normalized UV-vis absorption spectra of C₁₀O-PPV, CN-PPV, and DiCN-PPV in chloroform solutions and films are shown in Figure 3. The peak wavelengths, cutoff wavelengths and optical bandgaps are summarized in Table 1, together with molecular weights of the three polymers. The first cyano substitution causes absorption peak wavelength to blue shift significantly from 483 nm for $C_{10}O$ -PPV to 435 nm for CN-PPV in solutions. The second cyano group only produces a blue shift of 3 nm. It is also noticed that DiCN-PPV and $C_{10}O$ -PPV have smaller red shift in optical absorption peak wavelength from chloroform solution to film than that of CN-PPV. In general, polar polymers have stronger interactions in the solid state and have larger red shifts in absorption from solution to solid. For examples, RSO2-substitued PPVs have larger red shift than C10O-PPV,²⁹ and S,S-dioxothienylenevi-



Figure 3. UV–vis absorption (top), PL spectra (middle) of $C_{10}O$ –PPV, CN–PPV and DiCN–PPV in solution and film, and PL spectra of blend films (bottom) of MEH–PPV:CN–PPV and MEH–PPV:DiCN–PPV. Neat polymer films were excited at their peak absorption wavelengths. Blend films were excited at 487 nm.

	$M_{\rm w}/M_{\rm n}~{\rm (kDa)}$	λ^{abs}_{max}/nm (eV) sol./film	$E_{\rm g}^{\rm opt}/{\rm eV}$ sol./film	$\lambda^{\rm PL}_{\rm max}/{\rm nm}$ sol./film	$E_{\rm red}/{\rm LUMO}~({\rm V/eV})$	$E_{\rm ox}/{\rm HOMO}~({\rm V/eV})$	$E_{\rm g}^{\rm el}~({\rm eV})$
$C_{10}O-PPV$	23/12	483/481 (2.57/2.58)	2.25/2.14	550/582	- /-2.91	- /-5.15	2.24
CN-PPV	14/7.5	435/556 (2.85/2.23)	2.39/2.14	559/639	-1.5/-3.29	1.00/-5.79	2.50
DiCN-PPV	14/6.1	432/444 (2.87/2.79)	2.43/2.36	597/571	-1.09/-3.70	1.38/-6.17	2.47
^a Chloroform v	vas used as the	solvent for the polymers.					

Table 1. GPC, Optical, and Electrochemical Characterization Results of the PPV Polymers^a

nylene-based conjugated polymers³⁰ have larger red shift than nonpolar C_{12} -polythienylenevinylene.³¹ In DiCN–PPV, the *cis* unit is polar; however, it is highly nonplanar and does not permit strong interchain interactions in the solid state.

Cyclovoltammic measurements were performed on CN–PPV and DiCN–PPV films coated on a Pt working electrode and the results are given in Table 1. Relative to HOMO and LUMO levels of CN–PPV, the second cyano group lowers the HOMO energy by 0.38 eV and the LUMO energy by 0.41 eV. As a result, DiCN–PPV is more difficult to oxidize, but is easier to reduce. The calculated electrochemical bandgaps of the two polymers are almost same, with $E_{\rm g}^{\rm el}$ of DiCN–PPV smaller by only 0.03 eV. Therefore, the second cyano group does not bring significant change to the bandgap, but, does lower the energies of the frontier orbitals.

Photoluminescence (PL) Study. PL spectra of the PPV polymer films are shown in Figure 3. The PL peak wavelengths are 564 and 640 nm for DiCN–PPV and CN–PPV, respectively. The peak position of CN–PPV is similar to that reported by Chen et al.²¹ Given the fact that the UV–vis absorption λ_{max} s are essentially same, it is surprising to find that the PL λ_{max} of CN–PPV is red-shifted by 76 nm from that of DiCN–PPV. The strong interchain interactions in CN–PPV is believed to be the major reason for the red shift of PL and the extended long wavelength tail in the UV–vis absorption spectrum.²¹ The presence of high content of *cis* dicyanoviny-lene in DiCN–PPV is apparently very effective in preventing π -stacking of DiCN–PPV.

PL quantum yields (PLQYs) of polymer chloroform solutions were measured by the optically dilute method.³² Rhodamine 101 in ethanol, which is known to have a quantum yield close to 1,33 was used as the reference standard. Concentrations of all solutions were controlled low so that absorbances of the solutions in a 1-cm cell were smaller than 0.1. Excitation wavelength of 500 nm was chosen for all solutions. Obtained PL intensities were corrected for detector sensitivity. Integration of corrected PL spectrum of each polymer was compared with that of the standard solution to yield the PLQY. The absolute PLQYs of the polymer films were not measured due to the lack of a film standard and an integration sphere. The relative PLQYs of the polymer films were obtained by comparing the integrations of PL spectra of polymer films after correction for source intensity and film absorbance. For each polymer film, the sample holder was adjusted to maximize PL intensity at emission peak wavelength. The results are listed in Table 2. It is noticed that PL of DiCN-PPV solution is very weak, as evident from its noisy PL spectrum in Figure 3, top. The calculated PLQY of DiCN-PPV solution is only 0.08, or 14% of that of $C_{10}O$ -PPV solution. Surprisingly, it became more fluorescent than $C_{10}O-PPV$ in film. Assuming that the PLQY of $C_{10}O$ -PPV film is one-third of its QY in solution as reported for MEH-PPV,³⁴ the PLQY of DiCN-PPV film is as high as 0.34, more than four times as high as QY of its solution. This phenomenon has been known for molecular dyes such as auramine O and malachite green.³⁵

 Table 2. Photoluminescence Quantum Yields of PPVs with

 Different CN Substitution

	C ₁₀ O-PPV	CN-PPV	DiCN-PPV
solution ^a	0.57-0.6	0.35-0.4	0.08
film^b	1	1.87	1.71

^{*a*}Chloroform was the solvent for three polymers. QYs are relative to that of Rhodamine 101 ethanol solution. ^{*b*}QYs are relative to $C_{10}O-PPV$.

and a *trans*-stibene dye with two cyano groups on the C==C moiety.³⁶ Report of such behavior for polymers has not found in the literature. In all these dye molecules, twisted phenyls groups are present and their free waggling motion in solutions provides fast nonradiative decay for the excited states. DiCN– PPV is a likely the first vinylene-based conjugated polymers in which *cis* C==C is present in high percentage (~35%) and phenyl groups attached to the *cis* C==C bonds behave similarly to the phenyls in those dyes.

DiCN-PPV as an Electron Acceptor or PL Quencher. CN-PPV has been shown to be a good electron acceptor for donor polymers such as MEH-PPVs.³⁷ We are interested in finding out how an additional CN group affects ability of DiCN-PPV as an electron acceptor. PL spectra of the blend films of 1:1 MEH-PPV and CN-PPV or DiCN-PPV were recorded with excitation at 487 nm and are shown in Figure 3. PL intensity of the MEH-PPV/CN-PPV film is quite weak and the peak wavelength (647 nm) matches the PL peak wavelength of pure CN-PPV. The PL of MEH-PPV is not completely quenched and appears as a shoulder peak at 580 nm. In the case of MEH-PPV:DiCN-PPV film, the PL of MEH-PPV is completely quenched and the residual DiCN-PPV emission is negligible (only 5.56% of that of MEH-PPV/ CN-PPV film). The PL quenching efficiency in MEH-PPV:DiCN-PPV film is greater than 99.5%, much more complete than that in MEH-PPV:CN-PPV film for which ~93% quenching was reported.³⁷ Since MEH–PPV cannot lose its excitation energy by energy transfer to DiCN-PPV, the quantitative PL quenching suggests that a nearly quantitative charge transfer from MEH-PPV to DiCN-PPV happened in the film when illuminated.

Photochemical Stability of PPVs. We are most interested in the photostability of DiCN–PPV (in comparison with CN– PPV and $C_{10}O$ –PPV) in the sunlight for outdoor applications. Xenon light was used as the light source since its spectrum is close to that of sunlight. A very high intensity (2200–2600 mW/cm², more than 20 times the normal one sun intensity -100 mW/cm²) was used so that the photostability test could be completed in a relatively short period of time. The thicknesses of all films were controlled to have peak absorbance between 0.6 and 0.7. Such optical thickness was chosen to minimize the effect of thickness on decay constant and to allow sufficient range of photoinduced absorbance change to be measured with accuracy. Absorption and PL spectra were recorded after each illumination and are shown in Figure 4. **Macromolecules**



Figure 4. Evolutions of UV–vis and PL spectra of $C_{10}O$ –, CN–, and DiCN–PPV with increasing (accumulated) illumination time. The excitation wavelengths are 477, 463, and 441 nm for $C_{10}O$ –PPV, CN–PPV, and DiCN–PPV, respectively.



Figure 5. Left: Absorbance and PL intensity as functions of (accumulated) illumination time of DiCN–PPV. Right: Photodegradation of $C_{10}O$ –PPV, CN–PPV, and DiCN–PPV films shown as semilog plots of peak PL intensity v.s. illumination time. The initial intensities were normalized. The PL intensity of DiCN–PPV film at 20 min (in the left plot) was used as the starting point for the semilog plot. The emission wavelengths are 581, 624, and 562 nm for $C_{10}O$ –PPV, CN–PPV, and DiCN–PPV, respectively.

Both the PL and absorbance of $C_{10}O$ -PPV disappeared in about 5 min, along with the disappearance of the film color in

the illuminated area. The absorption peak gradually shifted to shorter wavelength as the illumination continued, presumably due to shortening of conjugation length with photodegradation. Blue shift of PL peak is not obvious since the emission from the sample would be dominated by remaining long polymer chains in the film due to the Förster resonance energy transfer³⁸ from shorter conjugated polymer chains to longer ones. CN–PPV film was more stable, but the original peak became unobservable in about 10 min. Its PL spectra were only shown up to 8 min of accumulated illumination time since absorption spectra after illumination for longer than 8 min were dominated by a new peak at 392 nm.

DiCN-PPV showed 17% increase in PL intensity in initial 20 min of illumination (Figure 5 left). The absorbance of the film (Figure 5 left) did not show any increase during the same period of time. Instead, it experienced faster decay in the first 3 min, as compared to its trend over the whole period of illumination. This fast decay period overlapped with the fast rise period of photoluminescence. The coincidence of the two observations can be explained by light-induced trans to cis isomerization which not only shortened conjugation length of the polymer and reduced polymer absorption, but also further disrupted packing of π -conjugated backbones and reduced interchain PL quenching. Semilog plots of peak PL intensity vs illumination time are shown in Figure 5 right for $C_{10}O-PPV$, CN-PPV and DiCN-PPV films. The initial intensities were normalized. The PL intensity of DiCN-PPV film at 20 min (in the left plot) was used as the starting point for the semilog plot since the changes in PL intensity during the initial 20 min were mainly caused by photoinduced trans-cis isomerization. All three plots can be fitted very well with a linear function of time, indicating a first-order decay for all three polymers. The slopes of the linear fittings are 0.239, 0.0249, and 0.0019 min⁻¹ for C10O-PPV, CN-PPV and DiCN-PPV films, respectively. So, with substitution of one cyano group, CN-PPV is more photochemical stable than $C_{10}O$ -PPV by 1 order of magnitude under the white light; with two cyano groups, DiCN-PPV is more stable than $C_{10}O$ -PPV by over 2 orders of magnitude.

4. CONCLUSION

A didecyloxy substituted poly(phenylenedicyanovinylene), DiCN-PPV, has been synthesized. The dicyano-substitued vinylene units exist in both trans and cis conformations in a ratio of about 65:35. It was found that the cis conformation could not be converted into trans conformation by acid treatment that worked for $C_{10}O$ -PPV. Study of a model compound for the diphenyl-substituted dicyanoethylene moiety of the polymer shows that cis and trans conformations coexist in equilibrium, indicating that the trans conformation is not much lower in energy than the *cis* conformation, in contrast to what have been observed for other PPV polymers.^{24,29} The unusually high cis content makes this polymer highly amorphous, very soluble in organic solvent, and highly fluorescent in the solid state with an estimated quantum yield up to 0.34. Interestingly, this polymer is only weakly fluorescent in solution presumably due to unrestricted waggling motions of out-of-plane phenyl groups bonded to the cis C=C. Illumination with white light induced certain degree of trans to cis conversion as evidenced by a reduction in light absorption, which was faster than the reduction caused by light-induced degradation. The lightinduced increase in cis content in turn caused a significant rise in photoluminescence of the DiCN-PPV film as a result of further reduction in interchain interaction. The two cyano group in DiCN-PPV brings a decrease of LUMO energy level by 0.79 eV, and makes the polymer more stable to intense

white light (>20 times as strong as the sunlight) than $C_{10}O-PPV$ by more than 2 orders of magnitude. The excellent photochemical stability and decently high fluorescence quantum yield in the solid state make DiCN–PPV a good candidate for outdoor fluorescent applications such as remote optical sensing.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based upon work supported by the U.S. Air Force Office of Sponsored Research under Award No. FA955010-1-0555. C.Z. is grateful to the support by the National Science Foundation through award 0931373 and the Department of Chemistry and Biochemistry and South Dakota NSF EPSCoR Program (Grant No. 0903804) for the startup funds. S.S. is grateful to the support by the Department of Defense through Award W911NF-06-1-0488. The authors would like to thank Ms. Liping Si and Dr. Hongshan He for assistant on the fluorescence measurements.

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