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Synthesis and Characterization of a Perylene-Based Luminescent Organic Glass

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Perylene diimide-based organic semiconductor materials have been the subject of investigation due to their advantageous photophysical and photochemical properties. Driving these studies are potential applications of perylene diimide derivatives in organic photorefractive media for optical signal processing,[1] electron-transporting components in organic light-emitting diodes,[2] semiconducting materials for electrophotography,[3] n-type photovoltaic materials for solar energy conversion,[4−6] fluorescent dyes,[7] and near-IR dyes.[8] Often, perylene derivatives are used as dopants in polymer composites, either as soluble components or dispersions. Poor solubility of perylene derivatives has spawned efforts to synthesize soluble analogues, facilitating use within a wider range of host matrices.

Recently, electroluminescent properties[9] and two-photon absorption[10,11] of a number of fluorene derivatives have been reported. The fluorene ring system is generally fluorescent and possesses high photochemical and thermal stabilities. To overcome solubility problems often associated with fluorene and perylene diimide derivatives, alkylation at various positions renders the derivatives soluble in organic solvents. High molecular weight organic glasses offer an alternative to guest/host polymer composites for the formation of amorphous thin organic films. We report the synthesis and characterization of a high molecular weight, florenyl perylene diimide derived glass that exhibits very good solubility in a number of organic solvents. Photoluminescence studies revealed perylene **2** undergoes intramolecular energy transfer from the fluorenyl moiety to the perylene ring system upon excitation with long wavelength UV light.

7-Benzothiazole-2-yl-9,9-didecylfluoren-2-ylamine (**1**)[12] was prepared in five steps from fluorene, full details of which will be reported elsewhere. The synthesis consisted of regiospecific mononitration, iodination, didecylation, Stille coupling of 9,9-didecyl-7-iodo-2-nitrofluorene and 2-(tri-*n*-butylstannyl)benzothiazole, and reduction of the nitro to the amine moiety with hydrazine hydrate and 10% Pd/C. Long alkyl groups at the 9-position were incorporated to enhance solubility. $Zn(OAc)_2$-catalyzed condensation[13] of 7-benzothiazole-2-yl-9,9-didecyfluoren-2-ylamine (**1**) and perylenetetracarboxylic dianhydride was accomplished by conducting the imidization reaction in quinoline at 160 °C for 20 h (Scheme 1). The resulting 2,9-bis(7-benzothiazol-9,9-didecylfluoren-2-yl)perylene diimide dye (**2**) was isolated in 70% yield as a deep red solid after column chromatographic purification (molecular weight = 1546 g/mol). The symmetrically substituted perylene-based dye, containing two didecyl fluorene moieties with the benzothiazole electron-withdrawing group, was fully characterized via conventional methods.[14] CHN analysis results were well within acceptable tolerances of calculated values, and the FT-IR spectrum revealed the presence of C═O stretching vibrations from the formed imide bonds at 1701 and 1665 cm^{-1}. The benzothiazole C═N stretching vibration at 1593 cm^{-1} was also observed.

Further structural determination was secured via ^{1}H and ^{13}C NMR spectroscopic analysis.[14] Obvious in the

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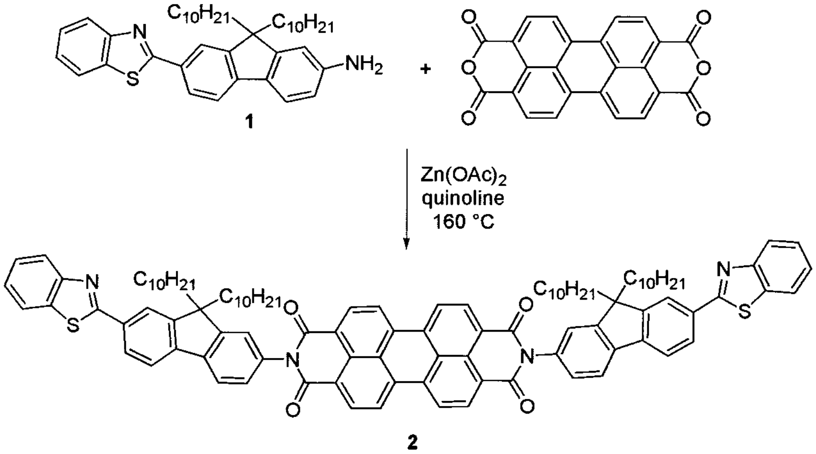
(12) 7-Benzothiazole-2-yl-9,9-didecylfluoren-2-ylamine (**1**): MS (EI, 70 eV) *m/z* 594 (M^+); 453 ($M - C_{10}H_{21}$); 327 ($M - C_{19}H_{39}$), 313 ($M - C_{20}H_{41}$); 163 ($C_{13}H_7^+$); 57 ($C_4H_9^+$), 43 ($C_3H_7^+$); UV−vis (THF) λ_{max} = 380 nm (210−450 nm); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.09, 8.05 (dm, 1H, ArH), 8.04 (d, 1H, ArH), 7.99, 7.95 (dd, 1H, ArH), 7.90, 7.86 (dd, 1H, ArH), 7.63, 7.59, 7.56, 7.51 (dd, 1H, ArH), 7.51, 7.44, 7.39, 7.32, (dq, 1H, ArH), 7.48, 7.35 (dm, 1H, ArH), 7.19 (m, 1H, ArH), 6.67 (M, 2H, ArH), 3.82 (bs, 2H, NH_2), 1.98 (m, 4H, CH_2), 1.15 (bm, 14H, CH_2), 1.04 (bm, 14H, CH_2), 0.82 (t, 6H, CH_3), 0.66 (m, 4H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$), tentative assignments based on calculated values, δ 169.3 (C7′), 154.5 (C13′), 153.8 (C2), 150.8 (C10), 147.1 (C13), 145.1 (C12), 131.6 (C7), 130.8 (C12′), 129.2 (C8), 128.4 (C4), 127.3 (C5), 126.4 (C6), 125.0 (C11), 123.0 (C10′), 121.5 (C9′), 121.5 (C11′), 118.8 (C8′), 114.3 (C1), 109.8 (C3), 55.4 (C9), 40.8 (Ca), 32.1 (Ch), 30.4 (Cc), 30.3 (Cd), 29.8 (Ce), 29.7 (Cf), 29.5 (Cg), 24.0 (Cb), 22.8 (Ci), 14.3 (Cj); FT-IR (KBr, cm^{-1}) 3741, 3383 (NH2), 2926, 2855 (alCH), 1460 (ArC═C), 1603 (C═N). Chemical shifts of ^{1}H and ^{13}C spectra were interpreted with the assistance of routines in CS ChemDraw Ultra version 5.0 by CambridgeSoft Corporation.

(13) Bohm, A.; Arms, H.; Henning, G.; Blaschka, P. WO97/22608, World Patent Application.

(14) ,9-Bis(7-benzothiazol-9,9-didecylfluoren-2-yl)perylenediimide (**2**): UV−vis (THF) λ_{max} = 345 nm (270−385 nm) and λ_{max} = 457, 486, and 522 nm (410−545 nm); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.80, 8.78 (d, 4H, ArH), 8.40, 8.30 (d, 4H, ArH), 8.60 (bm, 6H, ArH), 8.57, 8.44 (dd, 2H, ArH), 8.38, 8.29 (dd, 2H, ArH), 7.97, 7.93 (dd, 2H, ArH), 7.90, 7.87 (dd, 2H, ArH), 7.60, 7.53 (dd, 2H, ArH), 7.49, 7.45 (dd, 2H, ArH), 7.80 (bm, 2H, ArH), 2.15 (bm, 8H, CH_2), 1.15 (bm, 28H, CH_2), 1.10 (bm, 28, CH_2), 0.90−0.60 (bm, 20H, CH_2, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$), tentative assignments based on calculated values, δ 169.0 (C2′), 163.0 (peryl. C1), 154.0 (C8′), 152.5 (C10), 152.2 (C13), 143.5 (C7), 140.4 (C11), 134.9 (C2), 134.5 (C7′), 134.1 (peryl. C18), 132.4 (C12), 131.1 (peryl. C15), 129.1 (peryl. C19), 127.8 (C4), 127, 3 (C5), 125.8 (C1), 125.1 (C5′), 123.8 (C4′), 123.4 (C3), 123.0 (peryl. C16), 121.8 (C6′), 121.5 (C3′), 121.1 (C8), 120.8 (C6), 55.8 (C9), 40.0 (Ca), 31.9 (Ch), 30.0 (Cc), 29.5, 29.3 (Cd, e, f, g), 23.9 (Cb), 22.6 (Ci), 14.1 (Cj); FT-IR (KBr, cm^{1}) 3058 (ArCH), 2920, 2848 (alCH), 1701, 1665 (C═O), 1593 (C═N). Anal. Calcd for $C_{104}H_{112}N_4O_4S_2$: 80.79% C, 7.30% H, 3.62% N, 4.14% S.; Found: 80.39% C, 7.37% H, 3.38% N, 3.81% S.

10.1021/cm000045z CCC: \$19.00

Scheme 1



^{1}H NMR spectrum of **2** was the complete disappearance of the NH_2 protons present in **1** at 3.82 ppm. There was also a pronounced downfield chemical shift observed for the fluorene protons on carbons 1 and 2 ortho to the imide nitrogen to 7.93 and 7.76 ppm, respectively, compared to the corresponding protons in **1** at 6.67 ppm. Also notable was the appearance of two doublets attributable to the eight protons of the perylene ring system (8.80−8.30 ppm). The ^{13}C NMR spectrum of **2** proved to be equally informative as the carbonyl carbon of the imide bond was observed at 163.0 ppm. Carbons 8 and 6, ortho to the imide in the fluorene ring of **2**, were shifted downfield to 121.0 and 120.6 ppm, respectively, compared to the corresponding carbons in **1** observed at 114.3 and 118.6, respectively. Carbon 12, para to the imide in the fluorene ring of **2**, was also shifted downfield (132.4 ppm) relative to the same carbon in **1** (125.0 ppm). Finally, resonances ascribable to perylene carbons were observed which were not present in **1**.

Interestingly, perylene dye **2** exhibited two strong, UV−visible absorption bands (Figure 1), one in the UV from 270 to 385 nm ($\lambda_{max} = 345$ nm) and another in the visible from 410 to 545 nm with λ_{maxima} at 457, 486, and 522 nm. The first absorption band is due to the fluorenyl groups, as it is similar to the absorption range exhibited by the amine **1** from 210 to 450 nm ($\lambda_{max} = 380$ nm), with an expected blue shift due to changing the electronic characteristics of the substituent from an electron-donating amino group to an electron-withdrawing imide. The observed blue shift correlates well with the absorption of a related fluorenylimide analogue (the adduct of **1** and 1,8-naphthalic anhydride) with $\lambda_{max} = 350$ nm. The absorption of **2** in the visible range is due to the central perylene diimide ring system. Perylene **2** exhibited high absorptivity, with molar extinction coefficients of 133 × 10^3 and 138 × 10^3 at 344 and 523 nm, respectively (7.8 × 10^{-6} mol/L in THF).

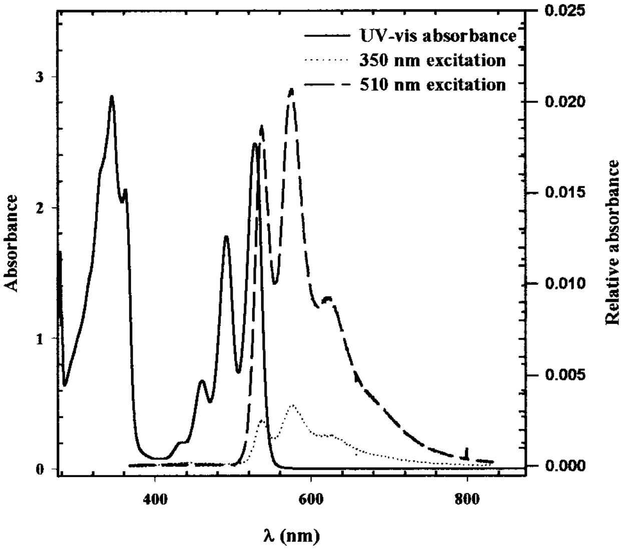


Figure 1. Overlay of UV−visible spectrum (solid line) and emission spectra of **2** excited at 350 nm (dotted line) and 510 nm (dashed line) in THF (2 × 10^{-5} mol/L).

Emission spectra of **2** were obtained and are shown in Figure 1, where excitation was performed at $\lambda_{ex} = 350$ nm, resulting in emission λ_{maxima} at 540, 585, and 625 nm. Meanwhile, excitation at $\lambda_{ex} = 510$ nm resulted in a similar emission λ_{maxima} profile as that obtained with the $\lambda_{ex} = 350$ nm.[15] The resulting emission profile from the first excitation is indicative of an intramolecular energy transfer process whereby the excited fluorenyl group undergoes energy transfer to the perylene ring system, facilitating excitation followed by emission.[16] This then generated a similar emission spectrum as that obtained from the $\lambda_{ex} = 510$ nm, although the relative intensity of the fluorescence from this energy transfer process is weaker than that of the corresponding fluorescence obtained from the excitation performed at the visible maxima due, presumably, to competing deactivation processes. The unsymmetrical nature of the emission is likely due to reabsorption of emission at 500−560 nm, since the Stoke's shift does not afford complete resolution of the absorption and emission spectra (the long wavelength absorption overlaps with the short wavelength emission).

Thermal analyses were performed on **2** to ascertain its thermal stability and properties, information important for elucidation of processing conditions. TGA analysis, performed under N_2 at a heating rate of 20

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[15] Photoluminescence experiments were performed using a 300-W Xe arc lamp, with quartz enclosure, excitation source (Oriel), and a Bausch and Lomb monochromator (1200 grooves/mm, pump resolution ~3 nm). The data were captured at 90° using an OMA 4000 (PARC) CCD array with 0.5-nm resolution.

[16] Kimura, M.; Shiba, T.; Muto, T.; Hanabusa, K.; Shirai, H. *Macromolecules* **1999**, *32*, 8237.

°C/min from room temperature to 650 °C, revealed **2** to exhibit high thermal stability up to 380 °C (~4% weight loss). A weight loss of 57% was subsequently observed between 380 and 650 °C, leaving a residue corresponding to 39% of the original sample weight. Repeated DSC scans with controlled heating and cooling were also performed on **2** under N_2 at a rate of 10 °C/min. The DSC analysis revealed a glass transition, T_g, onset at 110 °C and T_g midpoint at 118 °C. No melting transition was detected up to 380 °C. Controlled cooling revealed an obvious transition from 111 °C to 90 °C that correlated with the T_g observed during the heating scan. The DSC trace indicated **2** behaved much like a glassy material would, in which no clear melting or crystallization transitions were detected.

A remarkable feature of **2** was its solubility in common organic solvents (e.g., $CHCl_3$, THF, CH_2Cl_2), due, in large part, to the decyl groups at the 9 position of the fluorene ring system, facilitating formation of amorphous thin films via solution casting. Results of fluorescence microscopic analysis of solution-cast or spin-coated films from THF solution were consistent with fluorescence spectroscopic measurements, i.e., excitation with 470−490- or 530−550-nm light produced uniform red emission across the films. Fluorenylamine **1** exhibited strong nondegenerate two-photon absorption over a broad femtosecond white light continuum probe beam spectral range (460−650 nm) with a 1210-nm femtosecond pump beam.[17] Thus, perylene **2**, with its two chromophoric moieties, is potentially useful as a multiphoton-induced broad band optical limiting material. For example, the two chromophore moieties should provide broad band two-photon absorption in the ranges of 600−770 nm and 820−1090 nm. Current efforts are directed at investigating the nonlinear absorption, fluorescence quantum yield, and electrochemical properties of **2**.

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