Provided for non-commercial research and education use. Not for reproduction, distribution or commercial use.



This article was published in an Elsevier journal. The attached copy is furnished to the author for non-commercial research and education use, including for instruction at the author's institution, sharing with colleagues and providing to institution administration.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright



Available online at www.sciencedirect.com





Synthetic Metals 157 (2007) 1034-1039

www.elsevier.com/locate/synmet

Synthesis and photophysical properties of multi-branched ethynyl fluorene-labeled molecules

Hu Xiaodan^a, Hong Suk Kim^a, Min Ju Cho^a, Jung-Il Jin^a, Young Min Kim^b, Young Wook Park^b, Byeong-Kwon Ju^b, Dong Hoon Choi^{a,*}

^a Department of Chemistry, Advanced Materials Chemistry Research Center, Korea University, Seoul 136-701, South Korea
^b Display and Nanosystem Laboratory, College of Engineering, Korea University, Seoul 136-701, South Korea
Received 14 May 2007; accepted 17 October 2007

Abstract

Two kinds of emissive multi-branched molecule based on an ethynyl fluorene were synthesized by cyclotrimerization method. An ethynyl fluorenelabeled three-armed molecule, DBFP was prepared and the other one, CzDBFP has carbazole terminal groups tethered to DBFP. Their absorption and photoluminescent properties were investigated. The spectral analyses indicate that the molecules bearing ethynyl fluorene moieties as a peripheral group can exhibit highly isolated photophysical properties. The multi-branched molecule, CzDBFP was mixed with 2-{2-[2-(4-diethylaminophenyl)-vinyl]-6-methyl-pyran-4-ylidene}-malononitrile (DCM1) with an optimum concentration. At the low concentration (0.3 wt%) of DCM1, white emission was observed by incomplete energy transfer process from an excited CzDBFP. At the high concentration (3.0 wt%), red emission was predominantly observed, which was attributed to an efficient Förster energy transfer process. © 2007 Elsevier B.V. All rights reserved.

Keywords: Multi-branched molecule; Absorption; Photoluminescence; Förster energy transfer

1. Introduction

The electroluminescent (EL) multilayer device structures are composed of a hole-transport layer (HTL), emitting layer (EML), and electron transport layer (ETL). In a multilayer device, the individual layer should be optimized to have the suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. By finetuning of those energy levels, many promising HTL materials in a multilayer device was suggested to enhance hole-injection and block the electron; thus, confine excitons formed in the EML [1,2].

A number of works in recent years demonstrates that conjugated dendrimers have potential to be candidates for a solution-processable method. The use of functional dendrimers or multi-branched molecules has been proposed for fabricating the functional layer in the EL device since they possess unique molecular architectures and characteristics to optimize the proper HOMO and LUMO energy levels by simple click

* Corresponding author. *E-mail address:* dhchoi8803@korea.ac.kr (D.H. Choi). chemistry [3–9]. They can be employed for carrier transporting materials and also as luminescent host materials in EL devices [10].

In this work we synthesized two kinds of ethynyl fluorenelabeled molecules through a cyclotrimerization reaction. An ethynyl fluorene-labeled three-armed molecule, DBFP was prepared and the other one, CzDBFP was also synthesized bearing carbazole terminal groups, tethered to DBFP. Their absorption and photoluminescent (PL) properties were investigated both in solution and film states. The spectral analyses indicate that the molecules bearing ethynyl fluorene moieties as peripheral groups exhibit highly isolated photophysical properties. Facile energy transfer process was utilized for achieving red and white emission at a proper concentration of 2-{2-[2-(4-diethylamino-phenyl)-vinyl]-6-methyl-pyran-4ylidene}-malononitrile (DCM1) in CzDBFP.

2. Experimental

2.1. Instrumental analysis

NMR spectra were collected on a Varian 400 MHz spectrometer with chloroform-*d* as solvent and tetramethylsilane

^{0379-6779/\$ -} see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.synthmet.2007.10.015

as an internal standard. Elemental analyses were performed on EA1112 (Thermo Electron Corp.) elemental analyzer. Time-of-flight mass spectrometry (MALDI-TOF) was performed using a Voyager-DE STR MADI-TOF (matrix; DHB) mass spectrometer. Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821^e instrument. Thermal gravimetric analysis (TGA) was conducted on a TGA2050 (TA instruments, Mettler) thermal analysis system under a heating rate of 10 °C/min.

In order to study absorption behavior, thin films were fabricated on quartz substrates as follows. The solution (2wt%) of multi-branched molecules in monochlorobenzene was filtered through an acrodisc syringe filter (Millipore 0.2 µm) and subsequently spin-cast on the quartz glass. The film was dried overnight at 100 °C for 48 h under vacuum. Absorption spectra of samples in solutions (chloroform, conc. 1×10^{-5} mol/L) and film states were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 190-1100 nm. The PL spectra were recorded by AMINCO-Bowman series-2 luminescence spectrometer. The redox properties of the synthesized compounds were examined by cyclic voltammetry (Model: EA161 eDAQ). The thin films were coated on a platinum plate using chloroform as a solvent. The electrolyte solution employed was $0.10 \,\mathrm{M}$ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in a freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV/s.

2.2. Synthesis

2.2.1. 1-(4-Ethynyl-phenyl)-ethanone, 1

To a solution of 4-iodoacetophenone (1.23 g, 5.0 mmol)in 15 mL of toluene was added 2-methyl-3-butyn-2-ol (2 mL, 1.75 mmol) and 5 mL of triethylamine. The solution was allowed to stir for 5 min at 45 °C under argon atmosphere. Then 0.1 g of Pd(PPh_3)_4 and 0.05 g of CuI was added to the mother solution. After 5 h stirring, the mixture was poured into saturated ammonium chloride aqueous solution. The aqueous layer was extracted with CH₂Cl₂ twice and the combined organic layers were dried over magnesium sulfate. The solvent was removed and the residue was purified by silica-gel column chromatography (ethyl acetate:hexane = 1:1) to provide 0.87 g of brown powder.

The powder was dissolved in 20 mL of 2-propanol and 0.5 g of NaOH was added to the solution. The mixture was stirred at 80 °C for 6 h and then, poured into water. The aqueous layer was extracted with CH₂Cl₂ twice and the combined organic layers were dried over magnesium sulfate. The solvent was removed and the residue was purified by silica-gel column chromatography (ethyl acetate:hexane = 1:2) to provide pale-yellow powder (0.45 g, 63%). Elemental analysis: calc. for C₁₀H₈O: C, 83.31; H, 5.59. Found: C, 83.38; H, 5.74. ¹H NMR (δ , ppm) (400 MHz CDCl₃): 2.59 (s, 3H), 3.24 (s, 1H), 7.56 (d, *J*=8.6 Hz, 2H), 7.79 (d, *J*=8.2 Hz, 2H).

2.2.2. 1-[4-(9,9-Dibutyl-9H-fluoren-2-yl-ethynyl)-phenyl]-ethanone, 2

To a solution of 1 (0.72 g, 5.0 mmol) in toluene (15 mL) was added 9,9-dibutyl-2-iodo-9H-fluorene (2.02 g, 5.0 mmol) and triethylamine (5 mL, 3.59 mmol). The solution was stirred for 5 min at 45 °C under argon atmosphere. Then 0.1 g of Pd(PPh₃)₄ and 0.05 g of CuI were added into it. After 5 h stirring, the mixture was poured into saturated ammonium chloride solution. The aqueous layer was extracted with CH₂Cl₂ twice, and the combined organic layers were dried over magnesium sulfate. The solvent was removed and the residue was purified by silica-gel column chromatography (ethyl acetate:hexane = 1:1) to provide white powder (1.41 g, 67%). Elemental analysis: calc. for C31H32O: C, 88.53; H. 7.67. Found: C, 87.49; H, 7.92. ¹H NMR (δ , ppm) (400 MHz, CDCl₃): 0.67–0.54 (m, 10H), 1.10-1.04 (m, 4H), 1.97 (t, J = 8.2 Hz, 4H), 2.61 (s, 3H), 7.34–7.32 (m, 3H), 7.70–7.51 (m, 6H), 7.94 (d, J = 7.8 Hz, 2H).

2.2.3. Synthesis of DBFP, 3

To a solution of 2 (0.84 g, 2.0 mmol) in anhydrous ethanol (30 mL) under nitrogen was added SiCl₄ (4.59 mL, 40 mmol) dropwise at 0 °C. After complete addition, the reaction mixture was heated to reflux for 4 h, whereby the color of mixture changed from black to yellow. Then the mixture was poured into saturated NH₄Cl solution. The suspension was extracted by ether and washed with brine. The organics were dried with MgSO₄. After removing the solvent under reduced pressure, the residue was purified by silica-gel chromatography (hexane:dichloromethane = 4:1) to yield 0.46 g of white powder (58%). Elemental analysis: calc. for C₉₃H₉₀: C, 92.49; H, 7.51. Found: C, 92.32; H, 7.62. m/z (MALDI-TOF) 1207.61 (*M*⁺ requires 1207.71). ¹H NMR (δ, ppm) (400 MHz, CDCl₃): 0.70-0.66 (m, 30H), 1.10-1.06 (m, 12H), 1.99 (t, J=8.2 Hz, 12H), 7.35-7.33 (m, 9H), 7.54 (s, 4H), 7.57 (s, 2H), 7.73-7.69 (m, 18H), 7.85 (s, 3H).

2.2.4. 9-(9,9-Dibutyl-7-iodo-9H-fluoren-2-yl)-9H-carbazole, 4

2,7-Diiodo-9,9-dibutylfuorene (2.65 g, 0.499 mmol) and carbazole (0.84 g, 0.50 mmol) were dissolved in 25 mL of dioxane in the presence of potassium tert-butoxide (1.5 g, 1.34 mmol) and copper iodide (20 mg, 1.05 µmol). To the solution was added 2-diaminocyclohexane (0.3 g, 0.26 mmol) and the reaction mixture was allowed to stir at 110 °C under nitrogen atmosphere for overnight. After cooling the mixture to room temperature, it was poured into water and extracted by dichloromethane (100 mL) twice. The combined organic layer was dried by anhydrous MgSO₄, and then the solvent was removed by evaporation. The product was purified by silica-gel column chromatography (hexane:dichloromethane = 5:1) to yield white powder (1.48 g, 52%). Elemental analysis: calc. for C₃₃H₃₂IN: C, 69.59; H, 5.66; N, 2.46. Found: C, 69.59; H, 5.82; N, 2.30. ¹H NMR (δ, ppm) (400 MHz, CDCl₃): 0.76–0.67 (m, 10H), 1.17–1.10 (m, 4H), 2.01–1.95 (m, 4H), 7.55–7.29 (m, 9H), 7.72 (J=6.3 Hz, 2H), 7.87 (d, J = 7.8 Hz, 1H), 8.17 (t, J = 7.9 Hz, 2H).

2.2.5. 1-[4-(9,9-Dibutyl-7-carbazol-9-yl-9H-fluoren-2-ylethynyl)-phenyl]-ethanone, 5

The synthetic procedure of **5** is similar to that of **2**. (yield: 64%). Elemental analysis: calc. for C₄₃H₃₉NO: C, 88.17; H, 6.71; N, 2.39. Found: C, 88.18; H, 6.72; N, 2.20. ¹H NMR (ppm) (400 MHz, CDCl₃): 0.75–0.71 (m, 10H), 1.16–1.10 (m, 4H), 2.02–2.00 (m, 4H), 2.62 (s, 3H), 7.32–7.30 (m, 2H), 7.45–7.40 (m, 4H), 7.67–7.54 (m, 6H), 7.77 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 8.6 Hz, 2H), 8.17 (d, J = 7.8 Hz, 2H).

2.2.6. Synthesis of CzDBFP, 6

The synthetic procedure for CzDBFP is similar to that of DBFP. Yield 62%. Elemental analysis: calc. for $C_{129}H_{111}N_3$: C, 90.96; H, 6.57; N, 2.47. Found: C, 90.99; H, 6.59; N, 2.16. *m/z* (MALDI-TOF) 1702.38 (*M*⁺ requires 1703.28). ¹H NMR (ppm) (400 MHz, CDCl₃), 0.79–0.70 (m, 30H), 1.18–1.14 (m, 12H), 2.07–2.03 (m, 112H), 7.94–7.32 (m, 51H).

3. Results and discussion

The synthesis of 2-iodo-9,9-dibutylfluorene and 2,7-diiodo-9,9-dibutylfluorene was performed by following the literature method [11].

The compounds **2** and **5** could be prepared by a simple onepot reaction involving Pd-catalyzed alkynylation of halogenated arene with 4-ethynylacetophenone under the condition of Sonogashira coupling reaction [12].

Our objective was to accomplish the trimerization reaction with two acetylated aromatic compounds (2 and 5) to generate two three-armed molecules. Trimerization of acetophenone derivatives, 2 and 5 by treatment with SiCl₄ in ethanol was attempted and furnished the molecules, 3 and 6 in 58-62% yield

without a complex mixture of product. The molecular structures of all the compounds were confirmed using ¹H NMR, elemental analysis, and matrix-assisted laser desorption/ionization timeof-flight mass spectrometry (MALDI TOF MS). The newly synthesized molecules were well soluble at room temperature in common organic solvents such as chloroform, THF, and chlorobenzene; further they were found to display good self-film forming properties.

By using DSC, the glass transition temperatures (T_{gs}) of the two molecules **3** and **6** were determined to be 115 and 173 °C, respectively. No discernible melting behavior was observed in the DSC thermograms of these molecules up to 250 °C. It was further confirmed that both molecules form a stable amorphous glass (see Fig. 1). As was expected, the high molar mass compound **6** also showed a clear glass transition behavior at around 173 °C, which is relatively high. It indicates that an incorporation of carbazole moieties into a ethynyl fluorene moiety is very effective for increasing T_g of the molecule. Compounds **3** and **6** were found to be thermally stable, having high decomposition temperatures ranging from 422 to 442 °C (see Table 1).

The PL and absorption spectra of **3** and **6** in solution states are shown in Fig. 2. In the solution state, **3** and **6** exhibit a maximum absorbance at 337(354) and 352 nm with extinction coefficients of 74,000, and 80,000 M^{-1} cm⁻¹, respectively. Progressive redshift of the absorption spectrum of **6** was found with the increase of effective conjugated length. It means that carbazole moieties increase the effective intramolecular conjugated length of the molecule.

The PL spectra in solution states of the two compounds are composed of featureless vibronic bands. Maximum emission peaks at 398 and 419 nm are observed in **3** and **6**, which are associated with emission from the ethynyl fluorene-based dendron.



Fig. 1. DSC (A) and TGA (B) thermograms of DBFP (3) and CzDBFP (6). (a) DBFP, (b) CzDBFP.

Table 1	
Measured and calculated parameters for DBFP and CzDBFP	

	<i>T</i> _g (°C)	<i>T</i> _d (°C)	Absorption (nm)		Emission (nm)		$\lambda_{cutoff} (nm)$	$E_{\rm HOMO}~({\rm eV})^{\rm a}$	E _{LUMO} (eV) ^b	$\Delta E_{\rm g}^{\rm opt} ({\rm eV})^{\rm c}$
			Solution	Film	Solution	Film				
DBFP	115	442	337 (354)	337 (357)	398	406	380	5.28	2.00	3.26
CzDBFP	173	422	352	354	419	421	405	5.25	2.19	3.06

^a HOMO = $(4.40 + E_{ox}^{onset})$.

^b LUMO = HOMO – $\vec{E_g^{opt}}$.

^c Estimated from the onset of absorption edge ($E_{g}^{opt} = 1240/\lambda_{onset}$).



Fig. 2. Absorption (solid lines) and PL spectra (dotted lines) of DBFP and CzDBFP in solution states. (a) DBFP, (b) CzDBFP.

The absorption and PL spectra of films of the two compounds are shown in Fig. 2. Films of 3 and 6 exhibit distinct absorption maxima at approximately 337 and 354 nm, respectively. One shoulder at 357 nm was also observed in the film of 3 that is likely due to a molecular interactive mode.

In film state, they showed similar spectral shapes and undergo an identical shift of the higher energy band at the absorption maxima of 18 nm. The PL spectra of the films of the two molecules are red-shifted with a structureless emission with respect to the corresponding solution spectrum. The red-shift of the PL spectrum in a film state can be explained by the fact that the molecules possess a wider distribution of conformations, including a more planar state which gives rise to a lower energy bandgap. However, the shift of emission band is relatively small, which indicates no significant intermolecular interaction between the molecules. As shown in Fig. 3, the characteristic blue emission from the isolated ethynyl fluorene-labeled dendron is clearly observed at 406 nm in 3. Compound 6 exhibited a broad and structureless emission band at approximately 421 nm. The synthesized molecules in film states did not show significant red-shift of the spectra implying no undesired intermolecular interaction, which is attributed to the isolation of photophysical properties.

The PL quantum yield (Φ_F) of samples of **3** and **6** in chloroform were measured with 9,10-diphenylanthracene as the



Fig. 3. Absorption (solid lines) and PL spectra (dotted lines) of DBFP and CzDBFP in film states. (a) DBFP, (b) CzDBFP.

reference standard (cyclohexane solution, $\Phi_{\rm F} = 0.9$). The PL quantum yields of the films were found to be $11 \pm 3\%$ and $13 \pm 3\%$, for **3** and **6**, respectively.

Electrochemical analysis was performed to determine the redox potentials of the synthesized compounds 3 and 6. Cyclic voltammograms (CVs) were recorded on a film sample, and the potentials were obtained relative to an internal ferrocene



Fig. 4. PL spectra of sample I (a) and sample II (b) in film states. *Sample I: CzDBFP with 3 wt% of DCM1, sample II: CzDBFP with 0.3 wt% of DCM1.



Scheme 1. Synthetic procedure of DBFP.

reference (Fc/Fc⁺). These CV scans showed quasi-reversible oxidation peaks. In acetonitrile, compounds, **3** and **6** have one quasi-reversible oxidation (E_{ox}^{onset}) at 0.88 and 0.85 V, respectively (see Table 1). Unfortunately, the reduction potentials were irreversible; therefore, we were unable to estimate their HOMO and LUMO energies accurately. In order to determine the latter, we combined the oxidation potential from the CV with the optical energy bandgap (E_g^{opt}) obtained from the absorption edge in an absorption spectrum. The HOMO levels of **3** and **6** were determined to be -5.28 and -5.25 eV, respectively. Since carbazole groups behave as electron donors, **6** have slightly lower HOMO level than that of **3**. The optical band gaps (E_g^{opt} s) of the two molecules were found to be 3.26 and 3.06 eV for **3** and **6**, respectively, as estimated from their UV–vis absorption edges (see Table 1).

Considering the suitable energy level [HOMO level at -6.0 to -5.0 eV; LUMO level at -2.0 to -3.0 eV] for hole-transport layer (HTL) in the multilayer structural EL device, these values are quite promising for utilizing them as a HTL

for efficient cascading carrier transport and electron blocking layer.

In order to examine the functions as host materials in LEDs, 2-{2-[2-(4-diethylamino-phenyl)-vinyl]-6-methylpyran-4-ylidene}-malononitrile (DCM1) was mixed into CzDBFP, 6 at two different concentrations in monochlorobenzene. Samples I and II contain 3.0 and 0.3 wt% of DCM1, respectively. Then, we fabricated thin films on a quartz substrate for taking PL spectra with the excitation at 360 nm. In Fig. 4, we can see the significant difference of the PL spectra of samples I and II. In the doped sample with DCM1, the intensity at 420-425 nm was suppressed drastically. And red emission at around 620 nm increases significantly. DCM1 is capable of electronic excitation via Főrster energy transfer from the host material. PL studies of the doped matrix demonstrated that a significantly high-energy transfer from CzDBFP to DCM1 is achieved. It can be explained that efficient energy transfer from a singlet and triplet state of carbazole moiety to DCM derivatives can enhance red emission in the DCM1-doped matrix. When



Scheme 2. Synthetic procedure of CzDBFP.

4. Conclusion

We have synthesized two emissive multi-branched molecules based on fluorene, synthesized by cyclotrimerization method. They can be employed for hole-transport materials rather than emitting materials as well as host materials for a red emitting EL device. Two molecules (**3** and **6**) exhibit very high thermal and environmental stabilities. The HOMO and LUMO energies of the synthesized molecules are well suitable for hole-transporting materials in a multilayer EL device. The absorption and PL spectra indicate that the molecules bearing ethynyl fluorene derivatives as peripheral groups can exhibit highly isolated photophysical properties. It can be considered that these ethynyl fluorene-labeled multi-branched molecules have good potential for white organic light-emitting devices optimizing the concentration of DCM1.

Acknowledgments

This research work was supported by 21st Century Frontier Research Program (F0004091-0000-00) and LG-Philips-LCD CO. Ltd (2007–2008). Particularly, D.H. Choi acknowledges the financial support by the Seoul R&BD Program (2007–2008).

References

- [1] H. Yan, B.J. Scott, Q. Huang, T. Marks, Adv. Mater. 16 (2004) 1948.
- [2] Y.H. Niu, B. Chen, S. Liu, H. Yip, J. Bardecker, A.K.Y. Jen, J. Kavitha, Y. Chi, C.F. Shu, Y.H. Tseng, C.H. Chien, Appl. Phys. Lett. 85 (2004) 1619.
- [3] P. Furuta, J. Brooks, M.E. Thompson, J.M.J. Fréchet, J. Am. Chem. Soc. 125 (2003) 13165.
- [4] T.W. Kwon, M.M. Alam, S.A. Jenekhe, Chem. Mater. 16 (2004) 4657.
- [5] S.-C. Lo, T.D. Anthopoulos, E.B. Namdas, P.L. Burn, I.D.W. Samuel, Adv. Mater. 17 (2005) 1945.
- [6] E.B. Namdas, A. Ruseckas, I.D.W. Samuel, S.-C. Lo, P.L. Burn, J. Phys. Chem. B 108 (2004) 1570.
- [7] C. Huang, C.-G. Zhen, S.P. Su, K.P. Loh, Z.-K. Chen, Org. Lett. 7 (2005) 391.
- [8] X.-H. Zhang, S.-H. Choi, D.H. Choi, K.-H. Ahn, Tetrahedron Lett. 46 (2005) 5273.
- [9] J.P.J. Markham, E.B. Namdas, T.D. Anthopoulos, I.D.W. Samuel, G.J. Richards, P.L. Burn, Appl. Phys. Lett. 85 (2004) 1463.
- [10] J.Y. Li, D. Liu, C. Ma, O. Lengyel, C.S. Lee, C.H. Tung, S. Lee, Adv. Mater. 16 (2004) 1538.
- [11] X. Hu, Y. Chuai, F. Wang, C. Lao, W.O. Luan, W. Baik, L. Huang, D. Zou, Jap. J. Appl. Phys. 45 (2006) 579.
- [12] K. Sonogashira, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 3, Pergamon, New York, 1991, pp. 521– 549.