Solution-processable organic fluorescent dyes for multicolor emission in organic light emitting diodes[†]

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Four novel fluorescent dyes, bis(difluorenyl)amino-substituted carbazole 1, pyrene 2, perylene 3, and benzothiadiazole 4, were synthesized by C-N cross-coupling with a palladium catalyst. These dyes are soluble in common organic solvents, and their uniform films were formed by spin-coating from their solutions. Their glass transition temperatures were sufficiently high (120–181 °C) to form amorphous films for organic light emitting diodes. These solution processable dyes exhibited strong photoluminescence (PL) in the film form (1: sky blue, 2: blue-green, 3: yellow, and 4: deep red). Optical and electrochemical properties of the compounds were investigated with photoelectron spectroscopy and cyclic voltammetry. The energy levels obtained from both measurements were in good agreement, and those levels were related to the electronic properties of the central core; the electron-donating carbazole compound showed the lowest ionization potential and the electronwithdrawing benzothiadiazole compound showed the largest electron affinity. Simple double layer devices were prepared with these fluorescent dyes as emitting layer and bis(2-methyl-8-quinolinolato) (4-phenylphenolato)aluminium(III) (BAlq) as a common hole blocking layer for each color. Electroluminescence colors were the same as those of the PL spectra in each compound. These multicolor electroluminescences show that these conjugated oligomers can be candidates for solution processable light emitting materials for OLEDs as well as conjugated polymers or dendrimers.

Introduction

Solution processes such as spin-coating, inkjet-printing, or spray-coating for organic light emitting diodes (OLEDs) are still fascinating due to their potential advantages for the production of large area devices at low cost, although dry deposition processes under vacuum are far ahead of solution processes from the commercialization point of view. Conjugated polymers have been extensively studied as solution processable emitting materials for OLEDs since 1990.1 Precise control of molecular weight, end-group structure, and regioregular structure of the conjugated polymers for OLED has been established, but it is not possible to *purify* structural defects in a polymer chain thoroughly. However, monodisperse conjugated oligomers are able to have no structural defects and better purity from conventional purification methods such as column chromatography, recrystallization, and sublimation, and they can show a high glass transition temperature and a good film forming ability. While fluorescent or phosphorescent dendrimers with well-defined molecular structure and monodisperse molecular weight have been developed for solution processed OLEDs,²⁻⁵ there have been few reports on the conjugated oligomers as solution processable electroluminescent dyes.⁶⁻⁹ In this research, we designed bis(difluorenyl)amino-substituted fluorescent dyes 1-4 as solution processable light-emitting dyes. In these

compounds, the emitting color can be easily controlled by a kind of central dye, and outer fluorene oligomers can sterically prevent excimer formation between the emitting cores in a neat film. Successive deposition of the hole-transporting layer and the emitting layer in solution processes is still difficult because of their solubility problems. Therefore these compounds are designed to contain triarylamine units to have both holetransporting and emitting properties. On the other hand, dry deposition of the electron transporting layer onto the solution processed emitting layer is much easier than using a wet process. For practical application, the electron transporting layer has to be common for each color pixel to be deposited without a shadow mask like the deposition of cathode metal. We used bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminium(III) (BAlq) as an common electron transporting layer in the same thickness for each emitting dye.

Results and discussion

Synthesis

Four fluorescent dyes 1–4 were synthesized by palladiumcatalyzed cross-coupling reaction between excess 2-(2'-bromo-9', 9'-diethylfluoren-7'-yl)-9,9-diethylfluorene and 3-amino-*N*ethylcarbazole for 1, 1-aminopyrene for 2, 3-aminoperylene for 3, and 4-amino-2,1,3-benzothiadiazole for 4 (Scheme 1). Their structures were fully characterized by ¹H-NMR spectroscopy, matrix-assisted laser desorption/ionization time-of-flight (MALDI) mass spectrometry (MS), and elemental analysis. All compounds were purified by column chromatography, and then thoroughly purified with a train sublimation for OLED

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DPPF = 1, 1'-Bis(diphenylphosphino)ferrocene

Scheme 1 Synthesis of the compounds.

application. These sublimable properties are one of the advantages of these materials compared with conjugated polymers from the purity point of view, because it is difficult to separate low molecular weight impurities having similar polarity to the target compounds by column chromatography. In practice, such impurities are regarded as detrimental to device stability.

Thermal and optical properties

Decomposition temperatures at 5 wt% loss of the compounds were over 400 °C from thermogravimetric analysis (TGA). Glass transitions appeared at 154 °C for 1, 142 °C for 2, 181 °C for 3, and 120 °C for 4 in differential scanning calorimetry (DSC) measurements. These results ensure that these compounds can be sufficiently amorphous films to be used in OLED devices. All the compounds are soluble in toluene, THF, and 1,2-dichroloethane, and their uniform films were formed by spin-coating from their solutions. UV absorption and PL spectra of the solutions and the films on a quartz substrate were measured. PL spectra of the films showed the emission color derived from the central dye (1: sky blue, 2: blue-green, 3: yellow, 4: deep red). The outer oligofluorene groups did not affect the emission color because they have a wider energy gap than that of the central dye. The π -conjugations of the fluorene groups and the central dye seem to not be fully delocalized. PL quantum efficiencies ($\Phi_{\rm film}$) of the films were determined by using an integrating sphere system

under nitrogen atmosphere. All the compounds except **4** showed higher Φ_{film} values than that of tris(8-quinolinolato)aluminium (Alq₃) film (22%) which was determined under the same conditions (Table 1).

Electrochemical properties

Ionization potentials (I_p) were measured by photoelectron spectroscopy.¹⁰ Compound 1 showed the lowest I_p due to the electron-donating properties of the carbazole group, and compound 2 showed the highest I_p due to the electronwithdrawing properties of the benzothiadiazole group. The order of I_p among the compounds is in good agreement with that of the redox potentials in anodic scan mode from cyclic voltammetry (CV) (Table 2). Generally, it is hard to measure electron affinities $(E_{\rm a})$ of organic compounds. The tentative $E_{\rm a}$ values were estimated from the difference of $I_{\rm p}$ and optical band gap ($E^{\rm OPT}$) which is obtained from the UV absorption edge of the film. The order of $E_{\rm a}$ values are also consistent with that of redox potentials in cathodic scan mode from CV. The energy diagrams are shown in Fig. 1. In particular, in the energy levels corresponding to the highest occupied molecular orbital (HOMO) level, the $I_{\rm p}$ and redox potential values of each compounds are very similar, compared with those in the energy levels corresponding to the lowest unoccupied molecular orbital (LUMO) level. These are because all the compounds have a common arylamine moiety

Table 1 Thermal and optical characteristics of compounds 1-4

			UV/nm (log ε)			PL/nm			
	$T_{\rm g}/^{\circ}{\rm C}$	$T_{\mathrm{d}5\%}/^{\circ}\mathrm{C}$	toluene	THF	film	toluene	THF	film (Φ (%))	EL/nm
1	154	471	368 (4.78), 406 (4.84)	317 (4.85), 368 (4.83), 406 (4.89)	318, 378, 401	445	467	461 (34)	459
2 3 4	142 181 120	452 487 448	396 (4.95) 398 (4.65), 494 (4.19) 348 (4.83), 378 (4.89)	394 (4.96) 398 (4.81), 489 (4.33) 349 (4 73) 379 (4 82)	324, 397 401, 498 320, 356, 380	480 550 643	508 584 673	491 (40) 571 (23) 643 (10)	490 572 635

 Table 2
 Electrochemical properties of compounds 1–4

	Ip/eV	$E_{\rm a}/{\rm eV}$	$E^{\rm OPT}{}_{\rm g}/{ m eV}$	$E^{\text{anode}}{}_{1/2}{}^{a}/\mathrm{V}$	$E^{\text{cathode}}{}_{1/2}{}^{b}/\mathbf{V}$	$E^{\mathrm{EC}}{}^{c}$ /V
1	5.29	2.48	2.81	0.11 (5.29)	-2.58 (2.60)	2.69
2	5.52	3.01	2.51	0.29 (5.47)	-2.33^{d} (2.85)	2.62
3	5.41	3.09	2.32	0.24 (5.42)	-2.12(3.06)	2.36
4	5.62	3.49	2.13	0.38 (5.56)	-1.89 (3.29)	2.27

^{*a*} In the parentheses, calculated HOMO energy levels (eV) based on the I_p of compound 1 are shown.^{*b*} In the parentheses, calculated LUMO energy levels (eV) based on the I_p of compound 1 are shown.^{*c*} Electrochemically obtained bandgap: $E^{EC}_{g} = E^{unode}_{1/2} - E^{cathode}_{1/2}$.^{*d*} Measured by differential pulse voltammetry. The redox wave of CV was irreversible.



Fig. 1 Energy diagrams of compounds 1–4 measured by photoelectron spectroscopy (solid lines) and cyclic voltammetry (dotted lines). The values in parentheses are the energy levels estimated by cyclic voltammetry.

resulting in similar HOMO levels, while the LUMO levels are derived from the different central dyes.

OLED performance

Light emitting devices with the configuration ITO/poly(3,4ethylenedioxythiophene) (PEDOT) : poly(styrene sulfonic acid) (PSS) (40 nm)/1-4 (50 nm)/BAlq (50 nm)/LiF (0.5 nm)/Al (100 nm) were fabricated. PEDOT:PSS and the emitting layer were deposited by spin-coating in open atmosphere. BAlq and LiF/Al layers were deposited by evaporation under vacuum successively using two independent vacuum chambers for BAlq and for LiF/Al. EL spectra of the compounds are in good agreement with the PL spectra of the films. The EL spectrum and

the Commission Internationale de L'Éclairage (CIE) chromaticity coordinate of compound 4 was dependent on current density. The EL spectrum of 4 showed another emission around 480 nm derived from BAlq under high current density (Fig. 2). These results suggest that a part of injected holes can go into the BAlq layer because the I_p value of 4 (5.62 eV) is close to that of BAlq (6.0 eV) and charge recombination partially occurred in the BAlq layer. Carbazole dye 1 showed the highest current density and luminance among the compounds in Fig. 3, probably because of better hole injection due to its high I_p and because of efficient electron blocking by its high E_a . Driving voltages and efficiencies of the devices are shown in Table 3. The red emitting device containing 4 exhibited the lowest external quantum efficiencies (EQE, η) among the devices. Current densities of 4 were as high as those of 2 and 3, but luminance values of 4 were lower than the others probably because of its lowest PL efficiency among the dyes. The EQE values around 1% of the other devices (1-3) are reasonably high in limited and same device configurations, which is using a common electron-transporting material in the same thickness for the different colors. Even the lowest EQE (0.60%) of 4 should be considered high because the theoretical EQE may be 0.625% if the out-coupling efficiency and the ratio of singlet and triplet excitons are 25% and the charge recombination ratio is 100%. Recently ratios of singlet and triplet excitons higher than 25% in fluorescent conjugated polymers, and theoretical calculations of the ratio in model conjugated oligomers have been reported.¹¹ Conjugated oligomers having relatively large molecular weights would be interesting as experimental model compounds to investigate the singlet-triplet exciton ratio.



Fig. 2 EL spectra (a) and CIE coordinates (b) under 1 mA cm⁻² (circles) and 25 mA cm⁻² (triangles).



Fig. 3 (a) Current density-voltage and (b) luminance-voltage plots of OLEDs with the different dyes 1-4.

Table 3 Turn-on voltages at 1 cd m^{-2} and efficiencies at 100 cd m^{-2} and 1000 cd m^{-2} of the devices

	$1 \text{ cd } m^{-2}$ E/V	100 cd m ⁻²			1000 cd m ⁻²				
Compound		E/V	$\eta/{ m lm}~{ m W}^{-1}$	$\eta/cd A^{-1}$	η (%)	E/V	$\eta/\mathrm{lm}~\mathrm{W}^{-1}$	η /cd A ⁻¹	η (%)
1	3.05	5.44	1.29	2.22	1.35	8.37	1.61	1.57	0.95
2	3.79	6.21	1.32	2.61	1.06	8.60	1.32	2.60	1.06
3	3.64	6.07	1.42	2.75	0.93	8.65	0.75	2.07	0.71
4	4.21	8.06	0.24	0.61	0.60	10.84	0.14	0.50	0.46

Conclusion

We have synthesized novel fluorescent dyes, bis(difluorenyl)amino-substituted carbazole, pyrene, perylene, and benzothiadiazole derivatives, via palladium catalyzed C-N coupling. These dyes are soluble in common organic solvents, and have sufficiently high glass transition temperatures (120-181 °C) to form amorphous films. The energy levels of the compounds were related to the electronic properties of the central core: the electron-donating carbazole compound showed the lowest ionization potential and the electron-withdrawing benzothiadiazole compound showed the largest electron affinity in the compounds. The emitting colors were also reflected from the central core in the dyes, and they ranged from sky blue to deep red. Simple double layer devices from a solution process showed the same emission colors as PL, and their external quantum efficiencies were around 1%. Multicolor emissions from conjugated oligomer dyes having well-defined structures were achieved in OLEDs fabricated from a solution process.

Experimental

Materials

2-(2'-Bromo-9',9'-diethylfluoren-7'-yl)-9,9-diethylfluorene and 3-aminoperylene were synthesized according to literature reports¹² and their synthesis details are described in ESI.† 3-Amino-*N*-ethylcarbazole, 1-aminopyrene and 4-amino-2,1, 3-benzothiadiazole were purchased from TCI Japan. Tris(dibenzylideneacetone)dipalladium and 1,1'-bis(diphenylphosphino)ferrocene were purchased from Sigma Aldrich Japan.

Measurements

The ¹H NMR spectra were measured in deuterated solvents with a JEOL ECX 400 MHz spectrometer. Elemental analyses were carried out in the Elemental Analysis Service, Yamagata University, Japan. MALDI mass spectra were recorded on a Applied Biosystems Voyager DE-Pro from dithranol in positive linear mode. Thermogravimetric analyses were performed on a SII EXSTAR 6000 and a TGA/DTA 62000. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC7. Ionization potentials were measured with photoelectron spectroscopy in air (PESA) using a RIKEN KEIKI AC-3. UV-visible absorption spectra were recorded as solutions in THF with a Shimadzu UV-3150 spectrometer. PL spectra were recorded using a Jobin Yvon Fluoromax-2 fluorometer. PL quantum efficiencies were measured with an integral sphere system Hamamatsu C9920-01 under nitrogen. Electrochemistry was performed using a BAS Electrochemical Analyzer 660B. All measurements were performed at room temperature on samples dissolved in dry benzonitrile with 0.1 M tetra-n-butylammonium tetrafluoroborate as the electrolyte. The sample concentration was 1 mM, and a platinum working electrode, platinum counter electrode in 0.1 M tetra-nbutylammonium tetrafluoroborate in the same solvent as used for the sample, and a Ag/0.01 M AgNO₃ in acetonitrile reference electrode were used. The scan rate was 100 mV s⁻¹. The solutions were deoxygenated with argon. The ferrocenium/ferrocene couple was used as standard. All potentials are quoted relative to the ferrocenium/ferrocene couple. The EL devices were fabricated on indium tin oxide (ITO) coated glass substrates, ultrasonicated sequentially in detergent, methanol, 2-propanol and acetone, and exposed to UV-ozone ambient for 20 min. A hole-injecting layer, PEDOT:PSS, was spin-coated onto the ITO substrates and annealed at 160 °C for 15 min under vacuum. The emissive layers were prepared by spin-coating from 1,2-dichloroethane solution. Layer thickness calibration was performed using a Dektak 3 surface profilometer. A BAlq layer was formed on the emitting layer by vacuum evaporation under 2×10^{-4} Pa. Lithium fluoride and aluminium were finally deposited under 1×10^{-3} Pa as a cathode through a shadow mask, and its active area was 5 \times 5 mm². The EL spectra were measured on a Hamamatsu photonic multichannel analyzer PMA-11. The current-voltage (I-V) characteristics and luminance were measured using a Keithley 2400 Source Meter and a Konika Minolta CS-200, respectively. External quantum efficiencies were calculated assuming a Lambertian emission pattern and considering all spectral features in the visible range.

1

mixture of 2-(2'-bromo-9',9'-diethylfluorene-7'-yl)-9,9-Α diethylfluorene (1.00 g, 1.92 mmol), 3-amino-N-ethylcarbazole (0.135 g, 0.642 mmol), sodium tert-butoxide (0.185 g, 1.93 mmol), tris(dibenxylideneacetone)dipalladium (29 mg, 0.032 mmol), 1,1'-bis(diphenylphosphino)ferrocene (36 mg, 0.065 mmol), and toluene (100 cm³) was degassed and placed under nitrogen, and then heated at 100 °C for 32 h. The mixture was allowed to cool to room temperature and then toluene was added. The organic layer was washed with water, dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a *n*-hexane : toluene mixture (2:1) as eluent to give 1 (0.39 g, 56%). ¹H-NMR (400 MHz, d₆-DMSO, ppm) δ 0.32 (12H, t, J = 7.25 Hz), 0.42 (12H, t, J = 6.8 Hz), 1.42 (3H, t, J = 6.8 Hz), 1.89–1.99 (4H, m), 2.06–2.23 (12H, m), 4.73 (2H, d, *J* = 6.3 Hz), 7.00 (2H, d, J = 8.2 Hz), 7.18 (1H, t, J = 7.5 Hz), 7.23 (2H, s), 7.35-7.38 (5H, m), 7.47-7.51 (3H, m), 7.64-7.93 (18H, m), 8.07, 8.08 (2H, s). MALDI-MS m/z Calcd: 1090.62 (100.0%), 1091.62 (89.6%), 1092.62 (39.5%), 1093.63 (11.6%), 1094.63 (2.5%). Found: 1090.26 (100%), 1091.32 (92%), 1092.24 (52%), 1093.30 (22%), 1094.34 (6%). Elemental Anal. Calcd for C₈₂H₇₈N₂: C, 90.23; H, 7.20; N, 2.57. Found: C, 90.15; H, 7.43; N, 2.48%.

2

mixture of 2-(2'-bromo-9',9'-diethylfluorene-7'-yl)-9,9-Α diethylfluorene (1.50 g, 2.88 mmol), 1-aminopyrene (0.209 g, 0.962 mmol), sodium tert-butoxide (0.277 g, 2.88 mmol), tris(dibenxylideneacetone)dipalladium (44 mg, 0.048 mmol), 1,1'-bis(diphenylphosphino)ferrocene (53 mg, 0.096 mmol), and toluene (200 cm3) was degassed and placed under nitrogen, and then heated at 100 °C for 32 h. The mixture was allowed to cool to room temperature and then toluene was added. The organic layer was washed with water, dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a n-hexane : toluene mixture (1 : 1) as eluent to give 2 (0.51 g, 48%). ¹H-NMR $(400 \text{ MHz}, \text{CD}_2\text{Cl}_2, \text{ppm}) \delta 0.34 (12\text{H}, \text{t}, J = 7.25 \text{ Hz}), 0.44 (12\text{H}, \text{t})$ t, J = 7.25 Hz), 1.89–1.98 (4H, m), 2.03–2.17 (12H, m), 6.90 (2H, s), 7.29–7.36 (8H, m), 7.54 (2H, d, J = 8.2 Hz), 7.61–7.65 (10H,

m), 7.74 (2H, d, J = 6.3 Hz), 7.75 (2H, d, J = 7.7 Hz), 7.90–8.22 (9H, m). MALDI-MS m/z Calcd: 1097.59 (100.0%), 1098.59 (91.2%), 1099.60 (41.6%), 1100.60 (12.4%), 1101.60 (2.7%). Found: 1097.66 (100%), 1098.68 (99%), 1099.64 (55%), 1100.63 (19%), 1101.82 (5%). Elemental Anal. Calcd for $C_{84}H_{75}N_1$: C, 91.84; H, 6.88; N, 1.28. Found C, 91.48; H, 7.50; N, 1.15%.

3

A mixture of 2-(2'-bromo-9',9'-diethylfluorene-7'-yl)-9,9diethylfluorene (2.57 g, 4.93 mmol), 3-aminoperylene (0.438 g, 1.64 mmol), sodium tert-butoxide (0.473 g, 4.92 mmol), tris(dibenxylideneacetone)dipalladium (75 mg, 0.082 mmol), 1,1'-bis(diphenylphosphino)ferrocene (91 mg, 0.164 mmol), and toluene (100 cm³) was degassed and placed under nitrogen, and then heated at 100 °C for 32 h. The mixture was allowed to cool to room temperature and then toluene was added. The organic layer was washed with water, dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a *n*-hexane : toluene mixture (3 : 1) as eluent to give **3** (0.51 g, 27%). ¹H-NMR (400 MHz, CD₂Cl₂, ppm) δ 0.34 (12H, t, J = 7.3 Hz), 0.42 (12H, t, J = 7.7 Hz), 1.89–1.98 (4H, m), 2.04–2.12 (12H, m), 6.97 (2H, s), 7.29–7.36 (9H, m), 7.49–7.87 (22H, m), 8.19 (2H, d, J =7.1 Hz), 8.24 (2H, d, J = 7.3 Hz). MALDI-MS m/z Calcd: 1147.61 (100.0%), 1148.61 (96.1%), 1149.61 (45.1%), 1150.62 (14.3%), 1151.62 (3.3%). Found: 1147.66 (100%), 1148.69 (106%), 1149.68 (67%), 1150.68 (27%), 1151.71 (8%). Elemental Anal. Calcd for C₈₈H₇₇N₁: C, 92.02; H, 6.76; N, 1.22. Found C, 91.42; H, 6.75; N, 1.26%.

4

A mixture of 2-(2'-bromo-9',9'-diethylfluorene-7'-yl)-9,9-diethylfluorene (0.78 g, 1.5 mmol), 4-amino-2,1,3-benzothiadiazole (76 mg, 0.50 mmol), sodium tert-butoxide (0.144 g, 1.5 mmol), tris(dibenxylideneacetone)dipalladium (23 mg, 0.025 mmol), 1,1'-bis(diphenylphosphino)ferrocene (0.139 g, 0.25 mmol), and toluene (200 cm³) was degassed and placed under nitrogen, and then heated at 100 °C for 32 h. The mixture was allowed to cool to room temperature and then toluene was added. The organic layer was washed with water, dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a *n*-hexane : toluene mixture (1 : 3) as eluent to give 4 (0.22 g, 43%). ¹H-NMR (400 MHz, d₆-DMSO, ppm) δ 0.34 (12H, t, J = 7.25 Hz), 0.39 (12H, t, J = 7.25 Hz), 1.89-1.97 (4H, m), 2.09-2.20 (12H, m), 7.05(1H, d, J = 2.2 Hz), 7.07 (1H, d, J = 1.8 Hz), 7.19 (2H, d, J = 1.8 Hz), 7.32 (1H, d, J = 6.3 Hz), 7.36–7.42 (4H, m), 7.47–7.50 (2H, m), 7.70–7.93 (18H, m). MALDI-MS m/z Calcd: 1031.5 (100.0%), 1032.5 (82.7%), 1033.5 (38.3%), 1034.5 (12.8%), 1035.5 (3.3%). Found: 1031.3 (100%), 1032.3 (96%), 1033.3 (61%), 1034.3 (25%), 1035.4 (9%). Elemental Anal. Calcd for C₇₄H₆₉N₃S₁: C, 86.09; H, 6.74; N, 4.07; S, 3.11. Found: C, 86.28; H, 6.96; N, 3.82; S, 2.78%.

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