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Synthesis and Luminescence Characteristics of Conjugated Dendrimers with 2,4,6-Triaryl-1,3,5-triazine Periphery

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ABSTRACT: We have synthesized conjugated dendrimer with triazine peripheries, and their luminescence properties were investigated. The dendrimers consist of dendritic triazine wedges for electron transport, distyrylbenzene core as an emitting moiety, and *t*-butyl peripheral groups for good processing properties. The dendrimers have LUMO values of about -2.7 eV possibly because of the triazine moiety with high electron affinity. Photoluminescence study indicates that energy transfer occurs from the triazine wedges to the stilbene bridge, and finally to the core chromophore units due to a cascade decrease of bandgap from the peripheral wedge to core moiety. Therefore, the emission wavelength was determined by the structure of the core unit. The energy transfer efficiency of distyrylbenzene-cored dendrimers was about 75 and 55% for Trz-1GD-DSB and Trz-2GD-DSB, respectively. A preliminary electroluminescence property also was investigated. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 254–263, 2006

Keywords: conjuated dendrimer; conjugated polymers; dendrimers; light-emitting diodes (LED); synthesis

INTRODUCTION

Since the discovery of electroluminescence in small organic molecules and conjugated polymer, tremendous efforts have been focused on the development of new organic and polymeric materials with high efficiency and stability due to their display applications.[1–7] Recently, dendrimers have attracted considerable attention for their potential use in organic light-emitting diodes.[7–17] In particular, Burn and coworkers re-

ported on the conjugated light-emitting dendrimers based on the phenylenevinylene structure.[18–23] Dendrimers have several unique aspects as a luminescent material. They can be synthesized in high purity with monodispersity in molecular weight just as low molecular weight species. In addition, just like polymers, a spin-coating is applicable for thin-film fabrication. The control of bandgaps of wedges and core units would provide an energy transfer route from the surface toward the core, thus the wavelength of the emitting light can be controlled by the core structure of dendrimers.[18,21] In this work, we synthesized conjugated dendrimers that consist of 2,4,6-triaryl-1,3,5-triazine wedges, dis-

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tyrylbenzene core as an emitting moiety. The triazine units are expected to play an important role in our conjugated dendrimer system due to their high electron affinity.[24–29] For most electroluminescent conjugated polymers, the injection and transport of holes predominate. Therefore, electron injection has to be boosted or a barrier to the passage of holes should be provided to enhance device efficiencies. For these purposes, an additional hole-blocking/electron-transport layer between the cathode and the organic light emitting layer is employed. The materials for hole blocking/electron-transporting layer include low molecular weight compounds or polymers of nitrogen heterocycles such as 1,3,4-oxadiazoles, 1,2,4-triazoles, and 1,4-quinoxalines.[30–33] Recently, in particular, Schmidt et al. reported that 1,3,5-*s*-triazine molecules and high polymers could be used as a material for hole-blocking/electron-transport layer.[25–27,34] To obtain multifunctional materials, rather than using additional multilayer, charge-transporting species can be covalently attached to the backbone of linear conjugated polymers.

Therefore, incorporation of 2,4,6-triaryl-1,3,5-triazine unit at the periphery of conjugated dendrimers would lower the LUMO level, and thus enhance electron injection into the conjugated dendrimer system. In addition, an energy gradient would be built within the dendrimer from the triazine periphery to the stilbene branch, and finally to the core, which would facilitate efficient directional energy transfer from the periphery to the core of the π-conjugated dendrimer.[35] Herein, we report the synthesis of π-conjugated dendrimers with triazine periphery and their luminescence characteristics.

EXPERIMENTAL

Materials and Instruments

Tetrahydrofuran (THF) and toluene were used after distillation under sodium and benzophenone. Anhydrous N,N'-dimethylacetamide (DMAC) and other chemicals from Aldrich were used as received. 1,4-Bis(4-*tert*-butylstyryl)benzene was synthesized by following a literature procedure.[36] ^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY INOVA 400 at 400 and 100 MHz, respectively. FTIR spectra were obtained using PerkinElmer System 2000 FRIR spectrophotometer. MALDI-TOF spectra were obtained using Voyager Biospectrometry time of flight mass spectrometer (Perspective Biosystem) operated at 25 kV accelerating voltage in reflector mode with positive ionization. Dithranol was used as the matrix. Elemental analysis data were obtained using CE Instrument EA 1110. Cyclic voltammograms (CV) were obtained using a potentiostat (EG and G PAR 273) with a data acquisition module. UV–vis spectra were recorded on Hewlett–Packard 8452A spectrophotometer. Photoluminescence spectra were measured using Simadzu RF-5301PC spectrofluorophotometer and ISS PCI photon-counting spectrofluorophotometer equipped with a photomultiplier tube (Hamamatsu R928) as a detector.

EL Characterization

ITO-coated glass plates were washed and treated by oxygen plasma prior to use as a substrate. On the top of the substrate, a poly (*N*-vinylcarbazole) (PVK) layer (M_w: 280,000) of 70 nm thickness was deposited by spin-coating from solution in monochlorobenzene at 2500 rpm and dried at 80 °C in vacuum oven for 2 h. The dendrimer solution in trichloroethylene (0.5 wt %) was subsequently spin-coated on to the PVK layer at spin speeds in the range of 1500–2000 rpm for 60 s. A 150-nm-thick Li:Al-alloy cathode was then vacuum-deposited on the dendrimer layer at 5×10^{-6} Torr. The electrical and luminescence characteristics of the device were measured by using a current/voltage source measurement unit (Keithly 236) and an optical power meter (Newport 1830C) connected to a photodiode (Newport 818-UV). EL spectra were obtained by using ISS PCI photon-counting spectrofluorometer equipped with a photomultiplier tube (Hamamatsu R928) as a detector.

Synthesis

Synthesis of 2,4-Dichloro-6-(4-vinylphenyl)-1,3,5-triazine (1)

A THF solution (60 mL) of freshly prepared 4-styrenyl magnesium bromide (13.5 g, 65 mmol) was slowly added into a THF solution (100 mL) of cyanuryl chloride (10.9 g, 58 mmol), which was in an ice bath. The reaction mixture was stirred at 0 °C for 8 h under nitrogen. After the removal of the solvent at reduced pressure, the crude product was purified by column chromatography over silica gel using hexane/methylene chloride (10:1, v/v) as an eluent to obtain **1** as a white solid. (Yield 14.9 g, 77%), mp 102 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.44 (d, $J = 11$ Hz, 1H, —Ph—CH=CH_2 cis), 5. 93 (d, $J = 17.6$ Hz, 1H, —Ph—CH=CH_2 trans), 6.77 (dd, $J = 11$ and 17.6, 1H, —Ph—CH=CH$_2$), 7.53 (d, $J = 8.8$ Hz, 2H, —Ph—), 8.45 (d, $J = 8.4$ Hz, 2H, —Ph—) ^{13}C NMR (100.64 MHz, CDCl$_3$) δ 117.59, 126.72, 130.23, 131.72, 135.78, 143.73, 171.87, 174.28; IR (KBr): $v = 3080$, 2982, 1842, 1805, 1605, 1520, 1494, 1423, 1385, 1313, 1105, 855, 803; MS (FAB) calcd for C$_{11}$H$_7$Cl$_2$N$_3$ 252.10, found 252 Anal. Calcd for C$_{11}$H$_7$Cl$_2$N$_3$: C, 52.41; H, 2.80; N, 16.67. Found: C, 52.65; H, 2.93; N, 16.61.

Synthesis of 2,4-Bis(4-tert-butylphenyl)-6-(4-vinylphenyl)-1,3,5-triazine (2)

An aqueous solution (2 M, 100 mL) of sodium carbonate was added to a toluene solution (150 mL) of a mixture of 2,4-dichloro-6-(4-vinylphenyl)-1,3, 5-triazine (19 g, 43 mmol), tetrakis(triphenyl-phosphine)palladium (0.5 g, 0.4 mmol), and 4-*tert*-butylphenylboronic acid (19 g, 104 mmol). The reaction mixture was then stirred at 80 °C for 16 h under nitrogen. After cooling, the product was extracted with methylene chloride and dried over anhydrous sodium sulfate. After removal of the solvent at reduced pressure, the crude product was purified by column chromatography over silica gel using hexane as an eluent. The product was further purified by recrystallization from methylene chloride/methanol (1:5, v/v) to give **2** as a white powder. (Yield 8.3 g, 43%), mp 160 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 1.41 (s, 18H, *t*-Bu), 5.39 (d, $J = 11$ Hz, 1H, —Ph—CH=CH_2 cis), 5.9 (d, $J = 17.6$ Hz, 1H, —Ph—CH=CH_2 trans), 6.82 (dd, $J = 11$ and 17.6, 1H, —Ph—CH=CH$_2$), 7.6 (d, $J = 8.8$ Hz, 6H, —Trz—Ph—tBu, —Trz—Ph—CH=CH$_2$), 8.68 (d, $J = 8.4$, 4H, —Trz—Ph—tBu), 8.73 (d, $J = 8.4$, 2H, —Trz—Ph—CH=CH$_2$); ^{13}C NMR (100.64 MHz, CDCl$_3$) δ 31.22, 35.10, 115.74, 125.57, 126.37, 128.76, 129.16, 133.68, 135.85, 136.43, 141.35, 155.95, 171.02, 171.47; IR (KBr): $v = 3045$, 2953, 2867, 1930, 1609, 1579, 1515, 1462, 1372, 1017. 917, 818; MS (MALDI-TOF) calcd for C$_{31}$H$_{33}$N$_3$ 447.61, found 448.84 [m+H]$^+$ Anal. Calcd for C$_{31}$H$_{33}$N$_3$: C, 83.18; H, 7.43; N, 9.39. Found: C, 83.48; H, 7.55; N, 9.49.

Synthesis of Trz-1GD-CHO

A DMAC solution of **2** (7 g, 15 mmol), 3,5-di-bromobenzaldehyde(1.79 g, 6.7 mmol), sodium carbonate(1.8 g, 16.9 mmol), 2,6-di-*tert*-butylcre-sol(1.5 g, 6.7 mmol), and *trans*-di(μ-acetato)bis [*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (60 mg, 0.07 mmol) was stirred at 130 °C for 24 h under nitrogen. After cooling, the solution was poured into a mixture of methylene chloride and distilled water. The organic layer was separated and filtered through silica gel. After removal of the solvent, the residue was precipitated into methylene chloride/methanol (1:5, v/v) to give Trz-1GD-CHO as a yellow solid. (Yield 5.91 g, 87%), mp 350 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 1.40 (s, 36H, *t*-Bu), 7.23 (d, $J = 16$ Hz, 1H, Trz—Ph—CH=CH—), 7.30 (d, $J = 16$ Hz, 1H, Trz—Ph—CH=CH—), 7.59 (d, $J = 8.4$ Hz, 8H, —Trz—Ph—tBu), 7.69 (d, $J = 8.4$, 4H, —Trz—Ph—CH=CH—), 7.84 (s, 1H, —CH=CH—Ph—CHO), 7.91 (s, 2H, —CH=CH—Ph—CHO), 8.67 (d, $J = 8.4$ Hz, 8H, —Trz—Ph—tBu), 8.75 (d, $J = 8.4$, 4H, —Trz—Ph—CH=CH—), 10.04(s, 1H, —Ph—CHO); ^{13}C NMR (100.64 MHz, CDCl$_3$) δ 31.22, 35.08, 125.58, 126.78, 126.83, 128.56, 128.76, 130.08, 130.53, 133.59, 136.10. 137.22, 138.43, 140.37, 156, 170.78, 171.43, 192.03; IR (KBr): $v = 2965$, 2869, 2805, 1702, 1609, 1578, 1514, 1371, 950, 810; MS (MALDI-TOF) calcd for C$_{69}$H$_{68}$N$_6$O 997.31, found 998.06 [m+H]$^+$ Anal. Calcd for C$_{69}$H$_{68}$N$_6$O: C, 83.10; H, 6.87; N, 8.43. Found: C, 82.50; H, 7.05; N, 8.13.

Synthesis of Trz-1GD-vinyl

A THF solution (10 mL) of potassium *tert*-butox-ide (7.5 mmol) was added to a THF solution (70 mL) of Trz-1GD-CHO (5.0 g, 5.0 mmol) and methyl-triphenylphosphonium iodide (3.04 g, 7.5 mmol). The reaction mixture was stirred at room temperature for 5 h under nitrogen. After removal of the solvent, the crude product was poured into a mixture of methylene chloride and water. The product mixture extracted in the organic layer was purified by column chromatography on silica gel using hexane/methylene chloride (1:1, v/v) as an eluent. Further purification was performed by precipitation into methylene chloride/methanol to give Trz-1GD-vinyl as a white solid. (Yield 4.3 g, 86%), mp 320 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 1.40 (s, 36H, *t*-Bu), 5.36 (d, $J = 11$ Hz, 1H, —Ph—CH=CH_2 cis), 5.89 (d, $J = 17.9$ Hz, 1H, —Ph—CH=CH_2 trans), 6.80 (dd, $J = 10$ and 16, 1H, —Ph—CH=CH$_2$), 7.32 (s, 4H, —Trz—Ph—CH=CH—), 7.56 (s, 2H, —CH=CH—Ph—CH=CH), 7.61 (d,

J = 8.4, 8H, —Trz—Ph—tBu), 7.69 (s, 1H, —CH=CH—Ph—CH=CH), 7.76 (d, J = 8.4, 4H, —Trz—Ph—CH=CH—), 8.71 (d, J = 8.4, 8H, —Trz—Ph—tBu), 8.77 (d, J = 8.4, 4H, —Trz—Ph—CH=CH—); ^{13}C NMR (100.64 MHz, CDCl$_3$) δ 31.44, 35.30, 117.07, 124.53, 124.72, 125.80, 126.91, 128.89, 128.98, 129.55, 130.24, 133.88, 135.90, 136.68, 137.87, 138.60, 141.23, 156.16, 171.13, 171.64; IR (KBr): v = 3024, 2962, 2870, 1607, 1580, 1515, 1371, 1016, 958, 811; MS (MALDI-TOF) calcd for C$_{70}$H$_{70}$N$_6$ 995.34, found 996.0 [m+H]$^+$ Anal. Calcd for C$_{70}$H$_{70}$N$_6$: C, 84.47; H, 7.09; N, 8.44. Found: C, 84.40; H, 7.31; N, 8.38.

Synthesis of Trz-2GD-CHO

A DMAC solution (50 mL) of Trz-1GD-vinyl (5.0 g, 5.0 mmol), 3,5-dibromobenzaldehyde (0.57 g, 2.1 mmol), sodium carbonate (0.57 g, 5.5 mmol), 2,6-di-*tert*-butylcresol (0.48 g, 2.1 mmol), and *trans*-di(μ-acetato)bis[o-(di-o-tolylphosphino) benzyl] dipalladium(II) (0.02 g, 0.02 mmol) was stirred at 130 °C for 48 h under nitrogen. After cooling, the mixture was washed with water and extracted with methylene chloride. The product mixture in organic layer was purified by column chromatography on silica gel using hexane/methylene chloride (5:1, v/v) as an eluent to yield Trz-2GD-CHO as a light brown solid. (2.4 g, 52%), mp 350 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 1.37 (s, 72H, t-Bu), 7.19 (s, 12H, —Trz—Ph—CH=CH— and Trz—Ph—CH=CH—Ph—CHO), 7.52–7.60 (22H, —Trz—Ph—tBu and —Ph—CH=CH—Ph—CH=CH), 7.67 (d, J = 8.4, 8H, —Trz—Ph—CH=CH—), 7.87 (s, 1H, —CH=CH—Ph—CHO), 7.91 (s, 2H, —CH=CH—Ph—CHO), 8.61 (d, J = 8.4 Hz, 16H, —Trz—Ph—tBu), 8.70 (d, J = 8.4, 8H, —Trz—Ph—CH=CH—), 10.02 (s, 1H, —Ph—CHO); ^{13}C NMR (100.64 MHz, CDCl$_3$) δ 31.21, 35.00, 124.51, 125.40, 126.61, 128.43, 128.76, 129.26, 129.51, 133.64, 155.717, 170.58, 171.17, 191.98; IR (KBr): v = 2962, 2867, 1704, 1607, 1579, 1511, 1410, 1370, 1266, 1190, 1107, 1017, 955, 856, 808 MS (MALDI-TOF) calcd for C$_{147}$H$_{142}$N$_{120}$ 2092.82, found 2093.81 [m+H]$^+$ Anal. Calcd for C$_{147}$H$_{142}$N$_{120}$: C, 84.37; H, 6.84; N, 8.03. Found: C, 84.01; H, 6.81; N, 7.81.

Synthesis of Trz-1GD-DSB

A THF solution (5 mL) of potassium *tert*-butoxide (1.25 mmol) was added to a THF solution (10 mL) of tetraethyl 1,4-phenylenebis(methylene)diphosphonate (0.09 g, 0.24 mmol) and Trz-1GD-CHO (0.5 g, 0.5 mmol). The solution was stirred at room temperature for 12 h under nitrogen. The product mixture was washed with water and extracted with methylene chloride. The organic layer was filtered through silica gel and dried over Na$_2$SO4. After the organic layer was concentrated, the residue was precipitated into a mixture of methylene chloride/methanol (1:1, v/v). The product was further purified by Soxhlet extraction with acetone and petroleum ether to give Trz-1GD-DSB as a yellow-green solid. (Yield 0.35 g, 71%) mp 354–360 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 1.40 (s, 72H, t-Bu), 7.15 (d, J = 16 Hz, 2H, —CH=CH—Ph—CH=CH—Ph—Trz), 7.36-7.40 (8H, —Trz—Ph—CH=CH—), 7.52 (s, 4H, —CH=CH—Ph—CH=CH—Ph—), 7.61 (d, J = 8.4 Hz, 16H, —Trz—Ph—tBu), 7.75-7.80 (14H, —Trz—Ph—CH=CH— and —Trz—Ph—CH=CH—Ph—), 8.02 (d, J = 16 Hz, 2H, —CH=CH—Ph—CH=CH—Ph—Trz—), 8.71 (d, J = 8.4, 16H, —Trz—Ph—tBu), 8.81 (d, J = 8.4, 8H, —Trz—Ph—CH=CH—); IR (KBr): v = 3024, 2961, 2870, 1924, 1607, 1578, 1506, 1370, 1018, 957, 857, 808; MS (MALDI-TOF) calcd for C$_{146}$H$_{142}$N$_{12}$ 2064.77, found 2065.62 [m+H]$^+$ Anal. Calcd for C$_{146}$H$_{142}$N$_{12}$: C, 84.93; H, 6.93; N, 8.14. Found: C, 84.30; H, 6.10; N, 7.90.

Synthesis of Trz-2GD-DSB

A THF solution (5 mL) of potassium *tert*-butoxide (5.4 mmol) was added to a THF solution (10 mL) of tetraethyl 1,4-phenylenebis(methylene)diphosphonate (0.06 g, 0.16 mmol) and Trz-2GD-CHO (0.8 g, 0.38 mmol). The solution was then stirred at room temperature for 48 h under nitrogen. The product mixture was washed with water and extracted with methylene chloride. The organic layer was filtered through silica gel and dried over Na$_2$SO$_4$. After the organic layer was concentrated, the residue was precipitated into a mixture of methylene chloride/methanol (1:5, v/v). The product was further purified by Soxhlet extraction with acetone and petroleum ether to give Trz-2GD-DSB as a yellow-white solid. (Yield 0.32 g, 45%), mp 360 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 1.33 (s, 144 H, t-Bu), 6.91–7.81 (s, 98 H, vinyl H, core —Ph—CH=CH—Ph—CH=CH—Ph—, —Trz—Ph—tBu and —Ph—CH=CH—Ph—CH=CH—
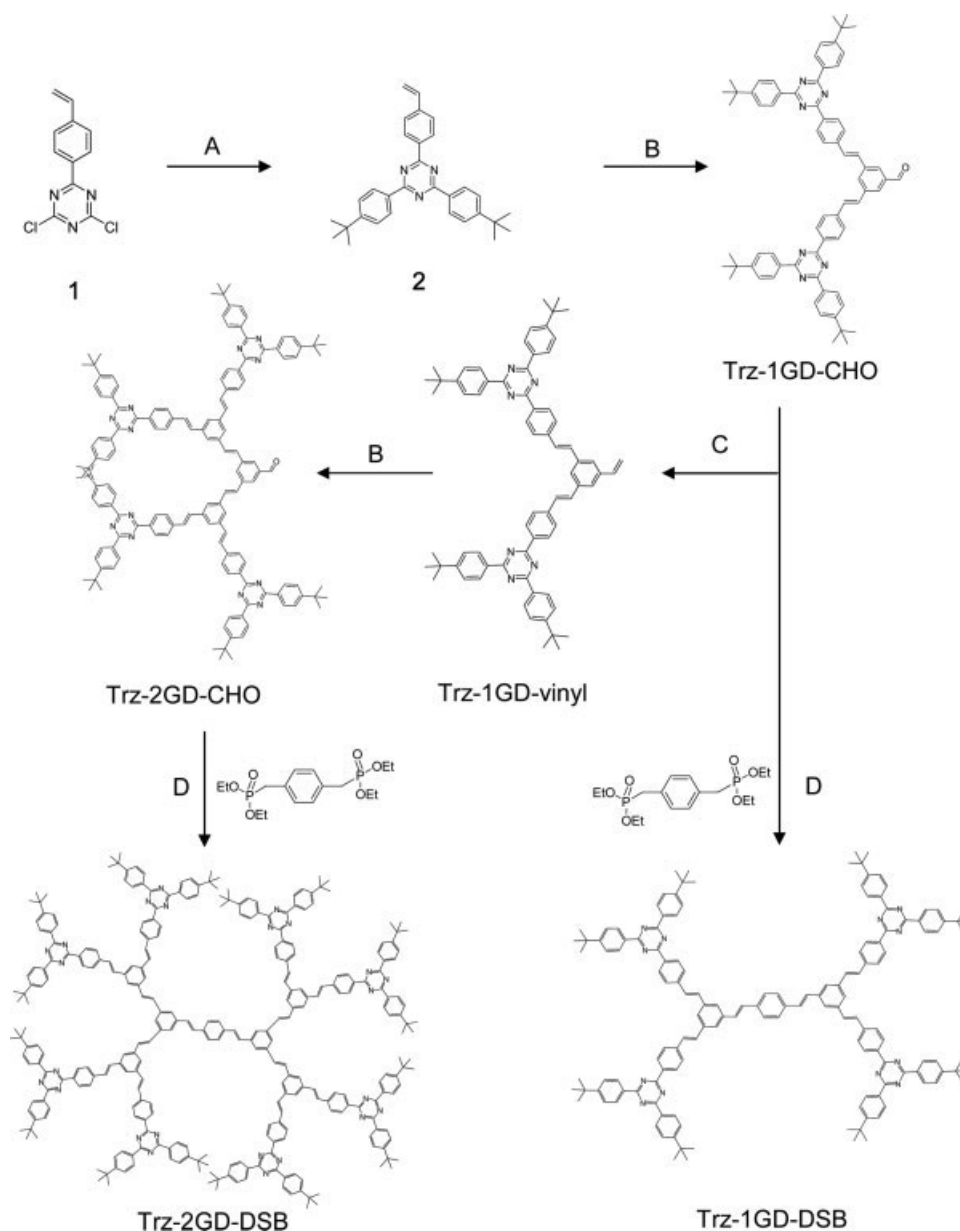
Scheme 1. Synthesis of dendrimers. (A) 4-*tert*-butylphenylboronic acid, Pd(PPh)$_4$, 2M Na$_2$CO$_3$, Toluene/H$_2$O (B) *trans*-di(μ-acetato)bis[o-(di-o-tolyphosphino)benzyl] dipalladium, Na$_2$CO$_3$, 3,5-dibromobenzaldehyde, DMAC (C) potassium *tert*-butoxide, methyltriphenylphosphonium iodide, THF (D) potassium *tert*-butoxide, THF.

Ph—), 8.36- 8.88 (s, 48 H, —Trz—Ph—tBu, —Trz—Ph—CH=CH—); ^{13}C NMR (100.64 MHz, CDCl$_3$) δ 31.22, 34.97, 125.11–126.09, 126.59, 128.70–130.17, 133.79, 135.34–136.32, 137.02–138.79, 155.27–156.39, 170.80–171.92 IR (KBr): v = 3026, 2961, 2867, 1607, 1578, 1512, 1409, 1369, 1266, 1191, 1107, 1016, 955, 856, 809 MS (MALDI-TOF) calcd for C$_{302}$H$_{292}$N$_{24}$ 4255.69, found 4256.67 [m+H]$^+$.

RESULTS AND DISCUSSION

Synthesis

The convergent synthetic route to the conjugated dendron and dendrimers with triazine periphery and chromophore core is described in Scheme 1. The selective reactivity of cyanuryl chloride toward Grignard reagent of p-bromostyrene at 0 °C provides an opportunity to yield
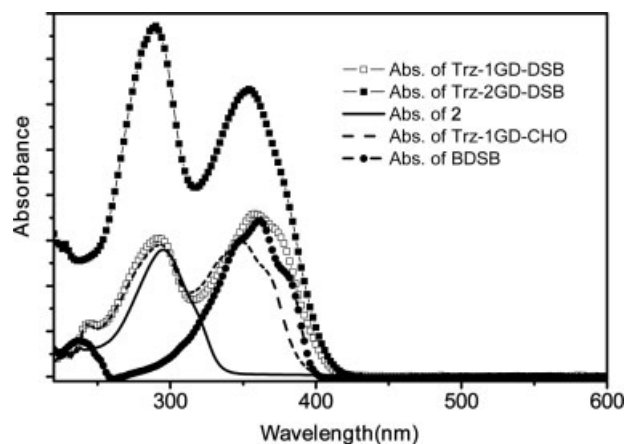
Figure 1. Absorption spectra of **2**, BDSB, Trz-1GD-CHO, Trz-1GD-DSB, and Trz-2GD-DSB in CH$_2$Cl$_2$.

monosubstituted triazine **1**, which was then converted to **2** by replacing the remaining two chlorine atoms with 4-*tert*-butylphenylboronic acid via Suzuki reaction.[37–39] The two-fold Heck reaction of **2** with 3,5-dibromobenzaldehyde produced first generation of the conjugated dendron Trz-1GD-CHO. The Heck reaction is the key to construct the dendritic branch with *trans*-stilbene moiety.[18] The next step was the vinylation of aldehyde-focalized dendron, Trz-1GD-CHO, to give Trz-1GD-vinyl via Wittig reaction with methyltriphenylphosphonium iodide. Then, iterative procedure of Heck reaction with dendron Trz-1GD-vinyl produced the second generation dendron, Trz-2GD-CHO. Finally, we have synthesized the dendrimers with distyrylbenzene (DSB) core, Trz-1GD-DSB and Trz-2GD-DSB, using Horner–Wadsworth–Emmons coupling, which is a selective reaction for the formation of trans carbon–carbon double bond.[40–43] For the synthesis of Trz-1GD-DSB and Trz-2GD-DSB, Trz-1GD-CHO and Trz-2GD-CHO were repectively coupled with tetraethyl 1,4-phenylenebis(-methylene) diphosphonate. The second generation dendrimer, Trz-2GD-DSB, was soluble in organic solvents such as methylene chloride, chloroform, and THF, while the first generation dendrimer, Trz-1GD-DSB, showed limited solubility in the same solvents. All the compounds were characterized by using ^{1}H and ^{13}C NMR, FTIR spectra, elemental analysis, and MALDI-TOF mass spectrometry.

Photophysical Characteristics

The absorption spectra of Trz-1GD-DSB (10^{-6} M) and Trz-2GD-DSB (10^{-6} M) in methylene chlor-

ide are shown in Figure 1. The absorption spectrum of Trz-1GD-DSB shows absorption maxima corresponding to each component of the dendrimer, that is 290, 352, and 370 nm, respectively, due to the triazine moiety, stilbene branch, and DSB core. This was confirmed by the absorption maxima of the model compounds such as **2** (290 nm) and 1,4-bis(4-*tert*-butylstyryl)benzene (BDSB) (370 nm). In case of the second generation dendrimer, Trz-2GD-DSB, the absorbance at 290 nm compared with that at 352 nm becomes stronger than in the first generation dendrimer, Trz-1GD-DSB, because of the increase of the number of triazine peripheral units. Furthermore, the absorption spectrum of Trz-2GD-DSB shows that the maximum absorption band at 370 nm assigned to the core DSB moiety of the dendrimer is completely covered by the increased absorption of the stilbene branch at 352 nm. These results show that the
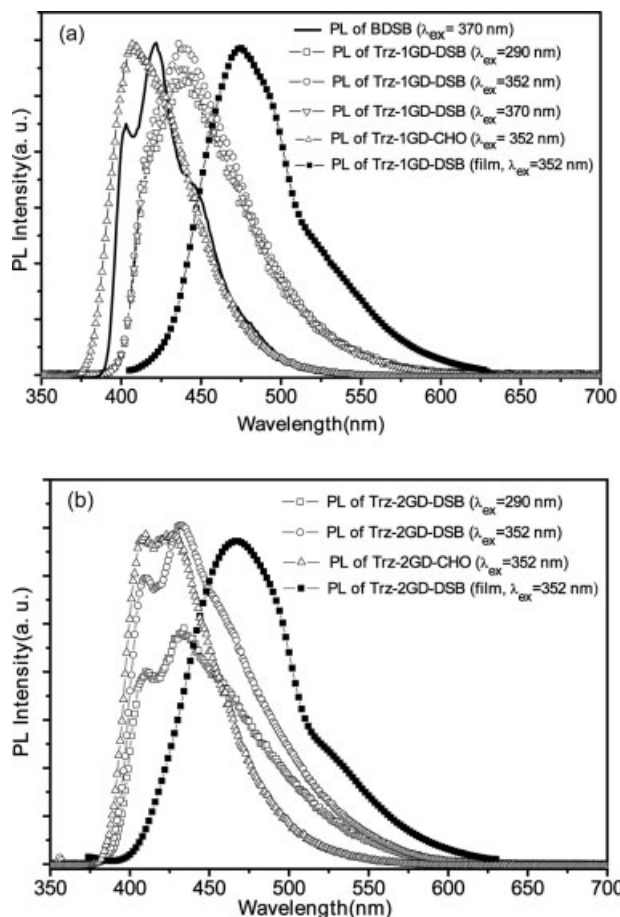

Figure 2. (a) PL spectra of Trz-1GD-DSB in CH$_2$Cl$_2$ and film. (b) PL spectra of Trz-2GD-DSB in CH$_2$Cl$_2$ and film.
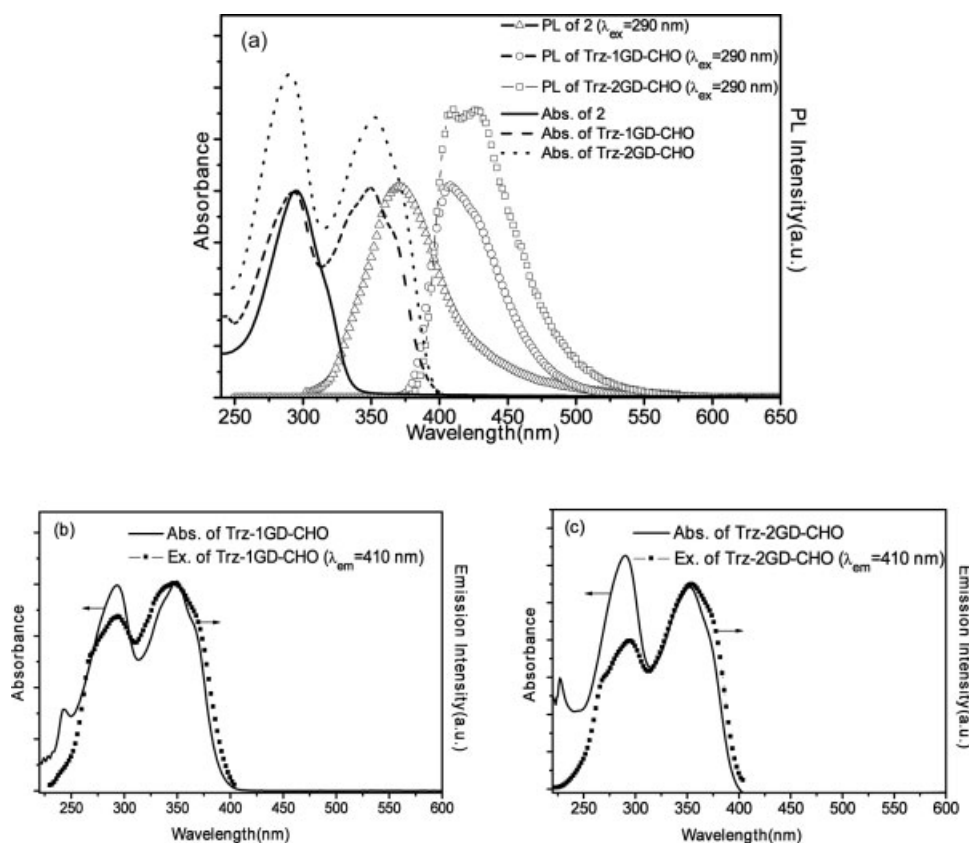
Figure 3. (a) Absorption and PL spectra of **2**, Trz-1GD-CHO and Trz-2GD-CHO in CH$_2$Cl$_2$. (b) Absorption and excitation spectra of Trz-1GD-CHO in CH$_2$Cl$_2$ (10^{-6} M). (c) Absorption and excitation spectra of Trz-2GD-CHO in CH$_2$Cl$_2$ (10^{-6} M).

absorption due to the dendritic branch and peripheral moiety, compared to that of the DSB core, increased in going from the first to second generation. The *meta*-branched dendrons disrupt π-electron conjugation between any pair of branches, and the electronic excitations are localized on each branch moiety.[44–46] This effect further allows only small amount of π-electron conjugation to be delocalized between the conjugated dendron wedge and the core chromophores.[7]

The PL spectra of Trz-1GD-DSB and Trz-2GD-DSB are shown in Figure 2. All the PL spectra of Trz-1GD-DSB (10^{-5} M) in methylene chloride excited at 290, 352, and 370 nm show the same emission maximum at 438 nm, which is due to the emission of the DSB core moiety [Fig. 2(a)]. There was no emission from triazine wegde or stibene branch moiety. This result suggests that the energy transfer occurs from the dendritic wedge to the DSB core moiety. The PL spectra of Trz-2GD-DSB (10^{-5} M) in methylene chloride excited at the absorption maxima (290

and 352 nm) exhibit the emission band at the identical wavelength of 432 nm, which is slightly blue-shifted compared to Trz-1GD-DSB [Fig. 2(b)]. The PL spectra of Trz-1GD-DSB (λ_{ex} = 352 nm) and Trz-2GD-DSB (λ_{ex} = 352 nm) as a thin solid film exhibit the emission band at 470 nm, which is red-shifted with respect to the solution PL possibly because of aggregation in the solid state.[7] To investigate the energy transfer characteristics of Trz-1G-DSB and Trz-2G-DSB, the photophysical properties of dendron Trz-1GD-CHO and Trz-2GD-CHO were studied. The absorption and PL spectra of **2**, Trz-1GD-CHO, and Trz-2GD-CHO in methylene chloride (10^{-5} M) are shown in Figure 3(a). The triazine compound 2 has the maximum of absorption at 290 nm and emission at 370 nm. The absorption bands of Trz-1GD-CHO at 290 and 352 nm are, respectively, due to 2,4,6-triaryl-1,3,5-triazine and stilbene branching units. The excitation of Trz-1GD-CHO at 290 or 352 nm exhibits the emission band at 410 nm, which is due to the stilbene moiety. The absence of the emission due
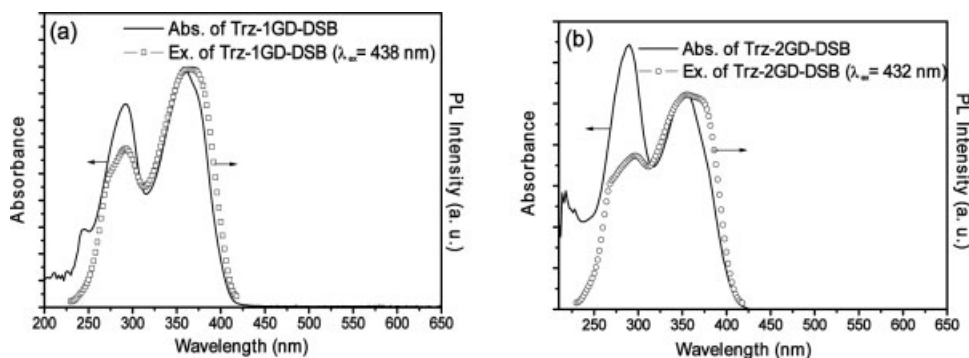
Figure 4. Absorption and excitation spectra of Trz-1GD-DSB in CH_2Cl_2 (10^{-6} M) (a) and Trz-2GD-DSB in CH_2Cl_2 (10^{-6} M) (b).

to the triazine unit at 370 nm when excited at 290 nm suggests that the energy transfer from the excited state of the triazine periphery to the stilbene branching moiety is efficient, which is further corroborated by the spectral overlap between the emission of the triazine unit (donor) and the the absortion of the stilbene moiety (acceptor). The absorption and PL property of Trz-2GD-CHO is similar to that of Trz-1GD-CHO as shown in Figure 3(a). The excitation of Trz-2GD-CHO at 290 nm or at 352 nm exhibits the emission band at 410 nm due to stilbene units. The excitation of Trz-2GD-CHO at 290 nm, similar to Trz-1GD-CHO, did not produce emission at 370 nm due to the triazine unit, which also suggests that the energy transfer occurs from the triazine periphery to the stilbene branching unit. By comparing the absorption and excitation spectra of the acceptor, the energy transfer efficiency was estimated to be about 85 and 60% for Trz-1GD-CHO and Trz-2GD-CHO, respectively [Fig. 3(b,c)].[47–50] This approach was also employed to get an idea of the efficiency of energy transfer in Trz-1GD-DSB and Trz-2GD-DSB from the triazine periphery to stilbene branches or distilbene core of the dendrimers. The efficiencies were estimated to be about 75 and 55% for Trz-1GD-DSB

and Trz-2GD-DSB, respectively, [Fig. 4(a,b)]. These results suggest that the cascade energy transfer occurs from the triazine periphery to the stilbene bridge, and finally to the distyrylbenzene core unit. And from the first to the second generation, the energy transfer efficiency decreased due to the increase of the distance between donor and acceptor.

The HOMO levels of the dendrimers were estimated by measuring the oxidation potential with cyclic voltammetry. The measurement was carried out on a Pt electrode in acetonitrile solution containing 0.1 M tetrabutylammonium tetrafluoroborate as electrolyte. A standard ferrocene/ferrocenium system was employed to calibrate the redox peaks. The HOMO levels were determined from the first oxidation potential value with respect to ferrocene with an Ag/AgCl reference electrode. The band gap was obtained from the absorption spectra (absorption edge) of the dendrimers as summarized in Table 1. The

Table 1. Energy Levels of Dendrimers

	Band Gap (eV)	HOMO (eV)[a]	LUMO (eV)[b]
Trz-1GD-DSB	3.04	−5.74	−2.70
Trz-2GD-DSB	3.03	−5.72	−2.69

[a] Estimated from the edge of absorption spectra.
[b] Estimated from the oxidation potential measured by cyclic voltammetry.
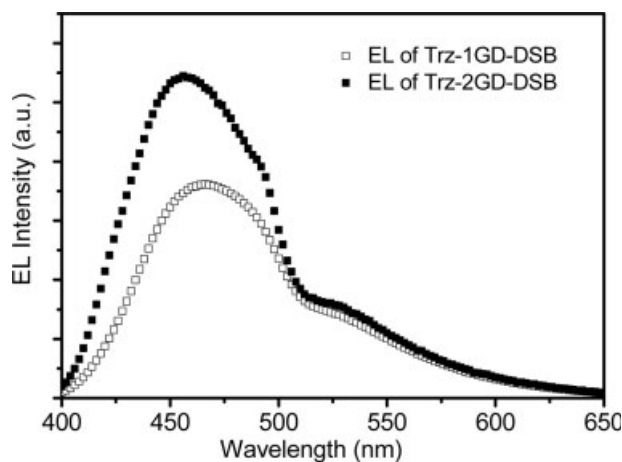

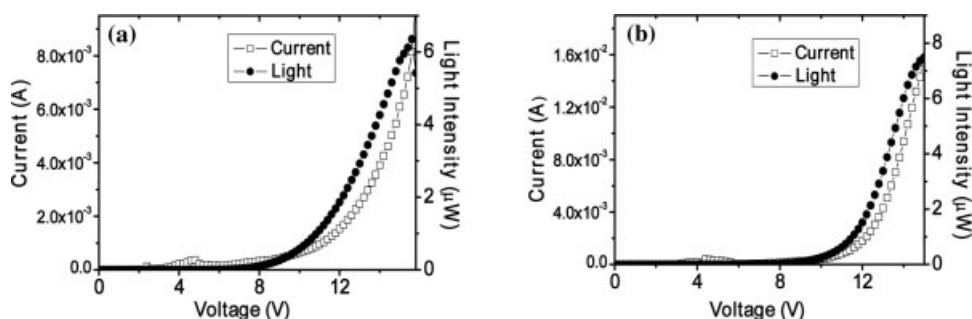**Figure 5.** EL spectra of Trz-1GD-DSB and Trz-2GD-DSB.

Figure 6. I-V-L curves of Trz-1GD-DSB (a) and Trz-2GD-DSB (b).

dendrimers have LUMO values of about −2.7 eV. This LUMO level is similar to that of 2,4,6-triphenyl-1,3,5-triazine (−2.71 eV), and is lower than that of 3,5-diphenyl-1,2,4-oxadiazole (−2.26 eV), which is known for electron transporting material.[27]

The EL spectra of Trz-1GD-DSB and Trz-2GD-DSB (shown in Fig. 5) were obtained by using PVK as a hole transporting layer, that is ITO/PVK/dendrimer/Al:Li. The spin-cast film had a thickness of a 100 nm controlled by the spin rate. The EL spectra of the dendrimers are similar to the corresponding PL spectra with emission maximum at 460 nm for Trz-1GD-DSB and Trz-2GD-DSB. Figure 6 shows the current–voltage–luminance (I-V-L) curves for the dendrimers. The turn-on voltages for Trz-1GD-DSB and Trz-2GD-DSB were 8.0 and 9.6 V, respectively. The external quantum efficiency was 0.047 and 0.031% for Trz-1GD-DSB and Trz-2GD-DSB, respectively. Higher efficiencies would be expected with optimization of the device structure.

SUMMARY

We have synthesized conjugated dendrimers that consist of the triazine periphery, stilbene branch units, and the distyrylbenzene core unit. Selective reactivity of the chlorine atoms of cyanuryl chloride provides an efficient route to the construction of conjugated dendrimers with triazine periphery with high electron affinity. The dendrimers have similar LUMO value of about −2.7 eV. Photoluminescence study showed that the emission came from the core chromophores due to a cascade energy transfer from the triazine periphery to the stilbene bridge, and finally to the core chromophore unit. From the first to second generation of dendrimer, the energy transfer efficiency decreased due to the increase of distance between donor and acceptor. The EL spectra of Trz-1GD-DSB and Trz-2GD-DSB showed emission maximum at 460 nm.

REFERENCES AND NOTES

1. Tang, C. W.; VanSlyke, S. A. Appl Phys Lett 1987, 51, 916.

2. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Nature 1990, 347, 539.

3. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A. D.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. Nature 1999, 397, 121.

4. Ho, P. K. H.; Kim, J.-S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. H. Nature 2000, 404, 481.

5. Cao, Y.; Parker, I. D.; Yu, G.; Zhang, C.; Heeger, A. J. Nature 1999, 397, 414.

6. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew Chem Int Ed Engl 1998, 37, 402.

7. Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. Adv Mater 1999, 11, 371.

8. Furuta, P.; Brooks, J.; Thompson, M. E.; Fréchet, J. M. J. J Am Chem Soc 2003, 125, 13165.

9. Lo, S.-C.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. Macromolecules 2003, 36, 9721.

10. Anthopoulos, T. D.; Frampton, M. J.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. Adv Mater 2004, 16, 557.

11. Tomalia, D. A.; Fréchet, J. M. J. J Polym Sci Part A: Polym Chem 2002, 40, 2719.

12. Fréchet, J. M. J.; J Polym Sci Part A: Polym Chem 2003, 41, 3713.

13. Lupton, J. M.; Hemingway, L. R.; Samuel, I. D. W.; Burn, P. L. J Mater Chem 2000, 10, 867.

14. Hecht, S. J Polym Sci Part A: Polym Chem 2003, 41, 1047.

15. Wang, H.; Li, Z.; Jiang, Z.; Liang, Y.; Wang, H.; Qin, J.; Yu, G.; Liu, Y. J Polym Sci Part A: Polym Chem 2005, 43, 493.

16. Vestberg, R.; Nilsson, C.; Lopes, C.; Lind, P.; Eliasson, B.; Malmström, E. J Polym Sci Part A: Polym Chem 2005, 43, 1177.

17. Tang, P.; Chuai, Y.; Cheng, C.; Xi, F.; Zou, D. J Polym Sci Part A: Polym Chem 2005, 43, 3126.

18. Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. Macromolecules 1999, 32, 5985.

19. Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Burn, P. L.; Bassler, H. Adv Mater 2001, 13, 258.

20. Pillow, J. N. G.; Burn, P. L.; Samuel, I. D. W.; Halim, M. Synth Met 1999, 102, 1468.

21. Halim, M.; Samuel, I. D. W.; Pillow, J. N. G.; Burn, P. L. Synth Met 1999, 102, 1113.

22. Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. Synth Met 1999, 102, 922.

23. Lupton, J. M.; Samuel, I. D. W.; Frampton, M. J.; Beavington, R.; Burn, P. L. Adv Funct Mater 2001, 11, 287.

24. Pang, J.; Tao, Y.; Freiberg, S.; Yang, X.-P.; DIorioa, M.; Wang, S. J Mater Chem 2002, 12, 206.

25. Inomata, H.; Goushi, K.; Masuko, T.; Konno, T.; Imai, T.; Sasabe, H.; Brown, J. J.; Adachi, C. Chem Mater 2004, 16, 1285.

26. Fink, R.; Heischkel, Y.; Thelakkat, M.; Schmidt, H.-W. Chem Mater 1998, 10, 3620.

27. Fink, R.; Frenz, C.; Thelakkat, M.; Schmidt, H.-W. Macromolecules 1997, 30, 8177.

28. Namazi, H.; Adeli, M. J Polym Sci Part A: Polym Chem 2005, 43, 28.

29. Acosta, E. J.; Gonzalez, S. O.; Simanek, E. E. J Polym Sci Part A: Polym Chem 2005, 43, 168.

30. Strukelj, M.; Miller, T. M.; Papadimitrakopoulos, F.; Son, S. J Am Chem Soc 1995, 117, 11976.

31. Kido, J.; Kimura, M.; Nagai, K. Science 1995, 267, 1332.

32. Kido, J.; Kimura, M.; Nagai, K. Chem Lett 1996, 25, 47.

33. Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. J Am Chem Soc 1996, 118, 3930.

34. Pösch, P.; Fink, R.; Thelakkat, M.; Schmidt, H.-W. Acta Polym 1998, 49, 487.

35. Devadoss, C.; Bharath, P.; Moore, J. S. J Am Chem Soc 1996, 118, 9635.

36. Verdal, N.; Godbout, J. T.; Perkins, T. L.; Bartholomew, G. P.; Bazan, G. C.; Kelley, A. M. Chem Phys Lett 2000, 320, 95.

37. Miyaura, N.; Suzuki, A. Chem Rev 1995, 95, 2457.

38. Cooke, G.; Cremiers, H. A. d.; Rotello, V M.; Tarbitc, B.; Vanderstraeten, P. E. Tetrahedron 2001, 57, 2787.

39. Takagi, K.; Hattori, T.; Kunisada, H.; Yuki, Y. J Polym Sci Part A: Polym Chem 2000, 38, 4385.

40. Meier, H.; Lehmann, M. Angew Chem Int Ed Engl 1998, 37, 643.

41. Diez-Barra, E.; Garcia-Martinez, J. C.; Rodriguez-Lopez, J. Tetrahedron Lett 1999, 40, 8181.

42. Wong, M. S.; Li, Z. H.; Shek, M. F.; Chow, K. H.; Tao, Y.; D'Iorio, M. J Mater Chem 2000, 10, 1805.

43. Wong, M. S.; Li, Z. H.; Shek, M. F.; Samoc, M.; Samoc, A.; Luther-Davies, B. Chem Mater 2002, 14, 2999.

44. Kopelman, R.; Shortreed, M.; Shi, Z.-Y.; Tan, W.; Xu, Z.; Moore, J. S.; Bar-Haim, A.; Klafter, J. Phys Rev Lett 1997, 78, 1239.

45. Tretiak, S.; Chernyak, V.; Mukamel, S. J Phys Chem B 1998, 102, 3310.

46. Melinger, J. S.; Pan, Y.; Kleiman, V. D.; Peng, Z.; Davis, B. L.; McMorrow, D.; Lu, M. J Am Chem Soc 2002, 124, 12002.

47. Stryer, L.; Haugland, R. P. Proc Natl Acad Sci USA 1967, 58, 719.

48. Mugnier, J.; Pouget, J.; Bourson, J.; Valeur, B. J Lumin 1985, 33, 273.

49. Gilat, S. L.; Adronov, A.; Fréchet, J. M. J. Angew Chem Int Ed Engl 1999, 38, 1422.

50. Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. J Am Chem Soc 2000, 122, 1175.