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Synthesis and Application of Dimeric 1,3,5-Triazine Ethers as Hole-Blocking Materials in Electroluminescent Devices

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A series of low molecular weight dimeric 1,3,5-triazine ethers with high glass transition temperatures is synthesized from 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine and various bisphenols. The thermal and electrochemical properties of these materials are examined using differential scanning calorimetry and cyclic voltammetry, respectively. The glass transition temperatures (T_g) are in the range of 106−144 °C, and all of them have similar thermal stability and show no weight loss up to 380 °C in thermogravimetric measurements. Some of these dimers form stable glasses which do not recrystallize on annealing at or above the T_g. Cyclic voltammetry studies reveal that these compounds undergo reversible reduction between −2.09 and −2.27 V vs ferrocene/ferrocenium as internal standard which correspond to LUMO values between −2.5 and −2.7 eV, respectively. The application of one of these dimeric ethers as a hole-blocking/electron-transport material in organic light-emitting devices is demonstrated.

Introduction

1,3,5-Triazines constitute a class of six-membered heterocyclics well-known through their application as melamine−formaldehyde resins and as materials with high thermal stability.[1] These materials are also employed as optical brighteners and as UV light-absorbing material for optical lenses and in photography.[2,3] A variety of materials such as low molecular weight compounds and dyes,[4,5] fully conjugated polymers,[6−8] polymers with fluorescent chromophores in the main chain or in the side chain,[9,10] segmented conjugated polymers,[11,12] and polymer blends[13−15] can be efficiently applied as electroluminescent (EL) materials. Chen and coauthors have reviewed the current developments in the design and use of low molecular weight EL materials recently.[16] However, most of these EL materials favor injection and transport of holes rather than electrons, and therefore, the recombination of charges takes place near the cathode resulting in quenching of the excitons produced. The use of an additional hole-blocking/electron-transport layer (HBETL) between the cathode and the organic layer helps not only to block the holes passing on to the cathode but also to inject electrons by tunneling effect, thus increasing the efficiency and stability of such devices. The most widely applied classes of materials are π-electron deficient heterocyclics carrying imine nitrogen atoms in the aromatic ring, such as 1,3,4-oxadiazoles, 1,2,4-triazoles, and 1,4-quinoxalines.[17−22] The use of various low molecular weight, oligomeric and polymeric heterocyclics as HBETL in

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organic light-emitting diodes (LEDs) has also been recently reviewed.[23] The properties such as high thermal and electrochemical stability along with relatively high electronaffinity and high ionization potential allow 1,3,5-triazines to be used as HBETL in electroluminescent devices. We have already demonstrated the applicability of aromatic poly(1,3,5-triazine ether)s as HBETL in two-layer electroluminescent devices with poly(*p*-phenylenevinylene) (PPV) as emitter resulting in increase of efficiency of such single layer PPV devices.[24] In this case, the poly(1,3,5-triazine ether)s were spin-coated on top of the insoluble PPV layer.

However, for use in multilayer LEDs fabricated by vapor deposition or by blending in a polymer matrix, amorphous low molecular weight compounds are needed. Some low molecular weight compounds such as oxadiazoles and triazoles have found an application as HBET material in multilayer LEDs.[17,25,26] Since 1,3,5-triazines have a comparatively higher electron affinity than 1,3,4-oxadiazoles and 1,2,4-triazoles,[27] low molecular weight triazines with sufficiently high glass transition temperatures should be suitable as HBET materials to be used in LEDs fabricated by vapor deposition or as blend in a polymer binder. With this aim, we synthesized low molecular weight dimeric 1,3,5-triazine ethers **3a**−**e** from 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (**2**) and various bisphenols. The spectroscopical characterization, thermal and electrochemical properties of these materials are also presented in this paper. The application of these dimeric ethers as HBETL in LEDs is demonstrated with **3b** as an example.

Experimental Section

Reagents and Materials. *N*-Benzamidine hydrochloride (Aldrich), 4-fluorobenzaldehyde (Fluka), and aniline (Aldrich) were used as received without further purification. *N*-Benzamidine was prepared by treating the corresponding hydrochloride with aqueous sodium hydroxide (30 wt %) followed by extraction with chloroform, drying with anhydrous Na_2SO_4, and evaporation of the organic phase under reduced pressure to dryness. 4,4′-(Isopropylidene)diphenol (bisphenol A), 4,4′-(hexafluoroisopropylidene)diphenol (hexafluoro-bisphenol A), 2,2′,6,6′-tetramethyl-4,4′-(isopropylidene)diphenol, 4,4′-(3,3′,5-trimethylcyclohexylidene)diphenol, 4,4′-(dodecanylidene)diphenol, poly(*N*-vinylcarbazole) (PVK), and tris(8-quinolinato)-aluminum(III) (Alq_3) were kindly supplied by Bayer AG, Krefeld, Germany. 1,3,5-tris{4-[di(4-ethylphenyl)amino]phenyl}-benzole (TDAPB) was obtained from Agfa-Gevaert N. V., RD Laboratories, Mortsel, Belgium. Dry DMF was puchased from Aldrich. Toluene, chloroform, and methanol were dried by common methods and distilled over Vigreux-columns.

4-Fluoro-*N*-benzylideneaniline or *N*-Phenyl-(4-fluorophenyl)methanimine (1). 4-Fluorobenzaldehyde (14.6 g, 120 mmol) and aniline (10.9 g, 120 mmol) were dissolved in chloroform and refluxed for 4 h in a Dean−Stark apparatus. At the end, solvent was removed with a rotary evaporator from the resulting yellow solution to give 21.9 g (110 mmol) of 4-fluoro-*N*-benzylidene (**1**, 92%). The purity was sufficient for the following synthesis step.

2-(4-Fluorophenyl)-4,6-diphenyl-1,3,5-triazine (2). Benzamidine (24.0 g, 200 mmol) and 4-fluoro-*N*-benzylideneaniline (19.9 g, 100 mmol) (**1**) were dissolved in 50 mL of dry DMF and heated at 80 °C for 24 h. The product was precipitated by cooling to room temperature and recrystallized from DMF to give 11.8 g (36.0 mmol) of 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (**2**) (36%, colorless needles). ^1H NMR: δ 7.2 (2 H_a), 7.6 (6 H), 8.8 (6 H) ppm. ^{13}C NMR: δ 115.6, 115.3, 128.5, 128.8, 131.0, 131.2, 132.2, 132.4, 135.9, 170.4, 171.4 ppm. FT IR (KBr): 3065, 1590, 1522, 1447, 1368, 1233, 744, 682, 644, 482 cm^{-1}.

1,3,5-Triazine Ethers 3a−e. 2-(4-Fluorophenyl)-4,6-diphenyl-1,3,5-triazine (**2**) (1.96 g, 6 mmol) and 2.5 mmol of the different bisphenols were dissolved in 100 mL of NMP/toluene (1:1 v/v) and refluxed with a stoichiometric amount of potassium carbonate in a Dean−Stark apparatus for 15 h for the removal of water formed. Toluene was distilled off, and the reaction mixture was stirred at 190 °C for 3 h. After cooling to room temperature, the solution was neutralized with dilute hydrochloric acid and poured dropwise into a 10-fold excess of methanol. The 1,3,5-triazine ethers **3a**−**e** were purified by precipitation from chloroform/methanol followed by extraction with ethanol for 6 h and filtration over silica gel. For **3a**: 1.71 g (2.0 mmol), yield 81%; ^1H NMR ($C_2D_2Cl_4$) δ 1.8 (s, 6 H), 7.1 (d, 4 H), 7.2 (d, 4 H), 7.3 (d, 4 H), 7.3 (d, 4 H), 7.6 (m, 12 H), 8.8 (m, 12 H) ppm; ^{13}C NMR ($C_2D_2Cl_4$) δ 30.8, 42.1, 117.6, 119.3, 128.1, 128.5, 130.2, 130.8, 132.4, 135.9, 146.4, 153.3, 161.5, 170.9, 171.2 ppm; FT IR (KBr) 3066, 2951, 1599, 1515, 1369, 1252, 1173, 833, 767, 692 cm^{-1}. For **3b**: 2.0 g (2.1 mmol), yield 85%; ^1H NMR ($CDCl_3$) δ 7.1 (d, 4 H), 7.2 (d, 4 H), 7.4 (d, 4 H), 7.6 (m, 12 H), 8.7 (m, 12 H) ppm; FT IR (KBr) 3068, 1595, 1517, 1369, 1247, 1182, 834, 770, 697 cm^{-1}. For **3c**: 1.6 g (1.9 mmol), yield 79%; ^1H NMR ($CDCl_3$) δ 1.8 (s, 1 H), 2.2 (s, 12 H), 7.0 (d, 4 H), 7.1 (s, 4 H), 7.6 (m, 12 H), 8.8 (m, 12 H); FT IR (KBr) 3065, 2948, 2865, 1590, 1519, 1368, 1241, 1170, 833, 769, 692 cm^{-1}. For **3d**: 1.6 g (1.7 mmol), yield 68%; ^1H NMR ($CDCl_3$) δ 0.5−2.7 (m, 15 H), 7.0 (d, 4 H), 7.1 (d, 4H), 7.4 (d, 4 H), 7.6 (m, 12 H), 8.7 (m, 12 H); FT IR (KBr) 3064, 2966, 2920, 1609, 1589, 1510, 1366, 1232, 1168, 834, 768, 691 cm^{-1}. For **3e**: 2.2 g (2.3 mmol), yield 91%; ^1H NMR ($CDCl_3$) δ 1.0−2.1 (m, 22 H), 7.1 (d, 4 H), 7.2 (d, 4 H), 7.6 (m, 12 H), 8.8 (d, 12 H) ppm; FT IR (KBr) 3064, 2959, 2924, 1613, 1588, 1511, 1359, 1235, 1172, 840, 766, 694 cm^{-1}.

Instrumentation. The structures of the compounds were confirmed by ^1H NMR (250 MHz) and ^{13}C NMR (62.5 MHz) spectroscopy using a Bruker AC250 spectrometer and by FTIR spectroscopy using a BIO-RAD Digilab FTS-40 spectrometer. Thermal characterization of the dimers was performed on a DSC 7 (Perkin-Elmer). Cyclic voltammetry measurements were carried out at a Pt electrode in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF) in acetonitrile or tetrahydrofurane using a three electrode cell and potentiostat assembly from EG&G Princeton Applied Research. The potentials were measured versus Ag/AgCl reference electrode with ferrocene (Fc) as internal standard according to literature.[28,29] Device characteristics of LED were measured with a multimeter Keithley 2000 and a progammable sourcemeter Keithley 2400 in a glovebox. Detection of electroluminescence was carried out with a photodiode UDT-PIN 10 DF calibrated with a Minolta LS 100 Luminometer.

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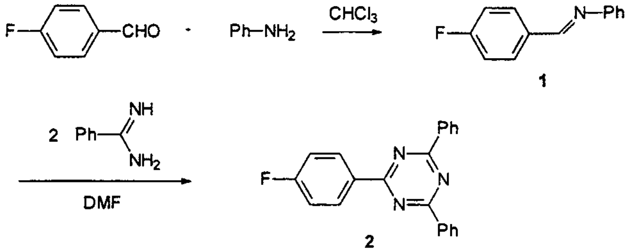
Scheme 1: Synthesis of 2-(4-Fluoro)phenyl-4,6-diphenyl-1,3,5-triazine (2)



Device Preparation. The hole transport layer (pure TDAPB or a blend of PVK + TDAPB + Alq_3 (4:1:1) was spin-coated on an ITO/glass substrate (sheet resistance 20 Ω/□) from a 1 wt % solution in 1,2-dichloroethane under an inert nitrogen atmosphere in a glovebox. The ITO substrates were purified by an oxygen plasma-etching process prior to use. Triazine ether **3b** (50 nm), Alq_3 (60 nm), and the magnesium/silver (by coevaporation at a rate of 10:1) were vapor deposited at $<10^{-5}$ mbar.

Results and Discussion

The symmetrically substituted 2,4,6-triaryl-1,3,5-triazines can be obtained by cyclization reactions of nitriles.[30–33] However, the unsymmetrically substituted diaryl and triaryl triazines which are interesting monomers for oligomerization/polymerization reactions can be obtained by the ring formation reaction of *N*-cyanoamidines and chloromethyleniminium salt[34] or by the reaction of benzamidines with benzoic acid anhydrides or Schiff bases.[35–37] We applied the latter method to synthesize the diaryl monofluoro-1,3,5-triazine **2** by the reaction of 4-fluoro-*N*-benzylideneaniline **1** and benzamidine[38] (Scheme 1). To study the influence of the spacer moiety on the solubility and thermal behavior of the 1,3,5-dimers, triazine **2** was attached to five different bisphenols. As outlined in Scheme 2, 1,3,5-triazine dimers **3a**–**e** were synthesized by nucleophilic displacement reaction of 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (**2**) and the various bisphenols in *N*-methylpyrrolidone (NMP)/toluene in the presence of potassium carbonate. The chemical structure of the dimers **3a**–**e** was confirmed by ^1H NMR spectroscopy and mass spectroscopy (see Experimental Section).

Thermal Characterization. Glass transition and melting temperatures of the synthesized 1,3,5-triazine dimers **3a**–**e** were determined by differential scanning calorimetry (DSC) at heating/cooling rate of 10 K/min. Thermal stability of the dimers **3a**–**e** was investigated by thermogravimetric analysis (TGA; heating rate 10 K/min, purge gas N_2). Table 1 summarizes the thermal properties of the synthesized bis[2′-(2,4,6-triphenyl-1,3,5-triazinyl)] ethers **3a**–**e**.

The bis[2′-(2,4,6-triphenyl-1,3,5-triazinyl)] ethers **3a**–**e** show glass transition temperatures between 106 and 144 °C. The highest glass transition temperature of 144 °C was observed for triazine dimer **3e**. The compounds **3a** exhibits melting endotherm at 145 °C in the first heating cycle. On cooling from melt, **3a** shows no recrystallization. In the subsequent heating cycle it shows only a glass transition at 106 °C, but no melting or recrystallization peaks were detectable. In the case of dimer **3b**, a glass transition as well as a melting point could be found in the first heating curve which is characteristic of semicrystalline compounds. The second heating curve of triazine **3b** shows only a glass transition. Obviously, triazine dimers **3a** and **3b** form metastable amorphous glasses. Tempering at or above glass transition temperatures results in recrystallization of triazine ethers **3a** and **3b**. In contrast to this, dimers **3c**–**e** exhibit exclusively glass transitions in the first and second heating curves. As an example, Figure 1 depicts the first and second heating curves for compounds **3b** and **3e** and also the first cooling curve for **3b**.

Table 1. Thermal Properties of the Bis[2′-(2,4,6-triphenyl-1,3,5-triazinyl)] Ethers 3a–e

triazine dimer	T_g (°C)[a]	ΔC_p (J/g °C)	T_m (°C)	ΔH_m (J/g)	T_{onset} (°C)[b]
3a	106	0.21	145[c]	30.94	461
3b	115	0.18	158[c]	25.33[d]	445
3c	139	0.19	*e*	*e*	416
3d	133	0.17	*e*	*e*	398
3e	144	0.17	*e*	*e*	397

[a] Second heating curve, heating rate 10 K/min. [b] Heating rate 10 K/min, purge gas N_2. [c] Only detectable at first heating curve. [d] Semicrystalline sample. [e] No melting was observed in the first and second heating curves between 20 and 300 °C.

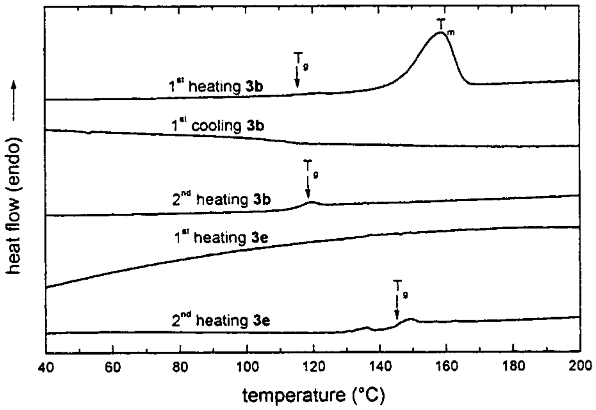


Figure 1. DSC curves of triazine dimers **3b** and **3e** (first and second heating curves and cooling at 10 K/min).

Recrystallization of triazine ethers **3c**–**e** could not be induced by tempering at or above glass transition temperatures. Therefore, we assume that triazine dimers **3c**–**e** form stable amorphous films. The thermal behavior of the triazine ethers **3a**–**e** can be explained as due to the influence of the bisphenol units. Substituents at the brigde carbon atom and the phenol cores influence glass transition temperatures as well as recrystallization tendency. Isopropylidene and hexafluoroisopropylidene groups possess more flexibility than cyclohexylidene or cyclododecanylidene groups. Four methyl substituents at the phenol units of compound **3c** prevent close packing of the molecules and hence crystallization as well. Therefore, dimers **3a** and **3b** tend to recrystallize, whereas triazine ethers **3c**–**e**

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Scheme 2: Synthesis of Bis[2′-(2,4,6-triphenyl-1,3,5-triazinyl)] Ethers 3a−e

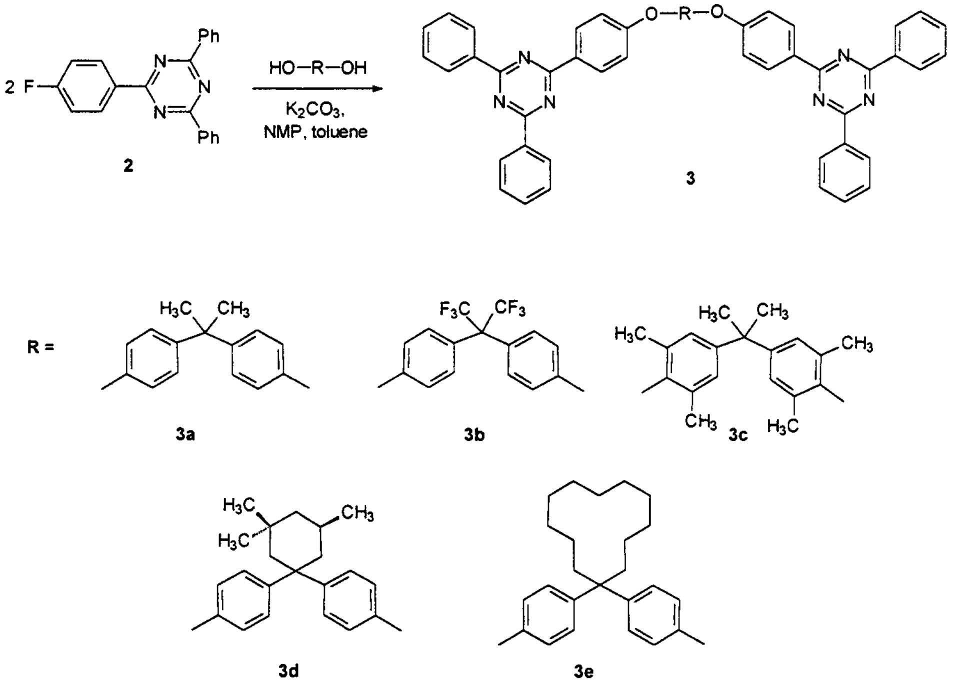


Table 2. Cyclic Voltammetry Data of Bis[2′-(2,4,6-triphenyl-1,3,5-triazinyl)] Ethers 3a−e and 2,4,6-Triphenyl-1,3,5-triazine (TRZ) Measured in 0.1 M Solution of Tetra(*n*-butyl)ammonium Hexafluorophosphate (TBAPF) in THF at a Scan Rate of 50 MV/s at 25 °C (Fc = Ferrocene)

triazine dimer	E_{red} vs Ag/AgCl (V)	E_{Fc} vs Ag/AgCl (V)	E_{red} vs Fc (V)	LUMO (eV)
3a	−1.65	0.62	−2.27	−2.53
3b[a]	−1.64	0.44	−2.08	−2.72
3c	−1.65	0.61	−2.26	−2.54
3d	−1.63	0.61	−2.24	−2.56
3e	−1.66	0.57	−2.23	−2.57
TRZ[a]	−1.65	0.44	−2.09	−2.71

[a] Measured in 0.1 M solution of TBAPF in acetonitrile.

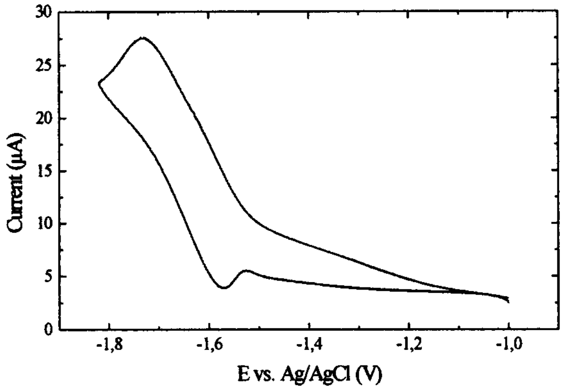
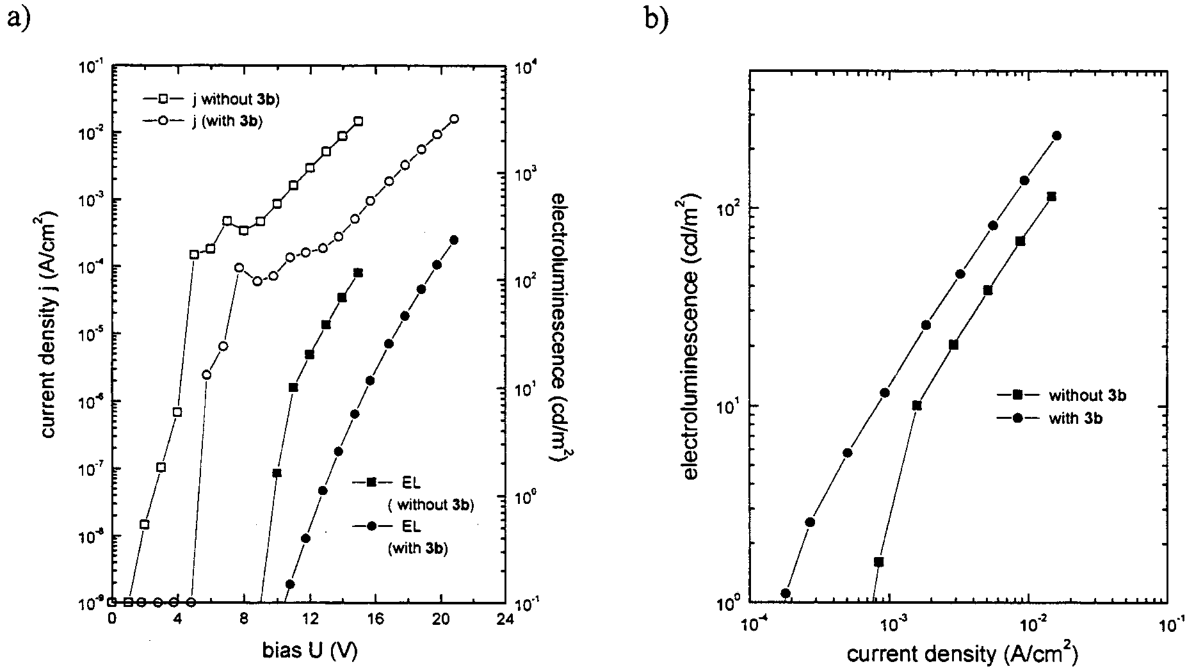


Figure 2. Cyclic voltammogram of **3a** measured at a Pt electrode in THF/0.1 M TBAPF at a scan rate of 50 mV/s at 25 °C.

form stable glasses. All compounds **3a**−**e** have similar thermal stability and show no decomposition up to 380 °C in TGA measurements.

Cyclic Voltammetry. The redox behavior of the bis-[2′-(2,4,6-triphenyl-1,3,5-triazinyl)] ethers **3a**−**e** was studied by cyclic voltammetry (CV). The characteristic data of triazine dimers **3a**−**e** measured at a Pt electrode versus a Ag/AgCl reference electrode at a scan rate of 50 mV/s at 25 °C are listed in Table 2. For comparison, the CV data of 2,4,6-triphenyl-1,3,5-triazine (TRZ) is also included. Each measurement was calibrated against an internal standard, the ferrocene/ferrocenium redox system.

TRZ exhibits one reversible reduction at −1.65 V vs Ag/AgCl in THF. Accordingly, two closely lying reductions are expected for dimers **3a**−**e**, first for the formation of radical anion followed by that for the dianion. However, the separation of potentials (Δ*E*) for anion and dianion depends on the interaction between the reduction centers and Δ*E* becomes almost negligible if the reduction centers are not at all conjugated. This was clearly observed in our CV measurements of perylene bisimides and triazole dimers. However, in the case of triazine dimers, only one reduction peak is observed indicating no interaction between the reduction centers in the molecule. Moreover, the dimers with the exception of **3b** undergo reduction at about −0.2 V higher than that for TRZ (all values measured vs Fc) which may be attributed to the electron-rich phenoxy groups in the dimers. In the case of **3b**, the electron-withdrawing hexafluoroisopropylidene group compensates for the phenoxy groups, and therefore, **3b** has almost the same value as that for TRZ. As an example, the cyclic voltammogram of **3a** is depicted in Figure 2. The LUMO energy values of the triazine dimers **3a**−**e** were calculated from their reduction potentials versus the internal standard, ferrocene/ferrocenium (Fc), according to the semiempirical method described by Daub et al. in the literature and are given as negative values with respect to the zero vacuum energy level.[28,29] For example, the triazine ether **3a** has a reversible reduction potential at −1.65 V vs Ag/AgCl. Fc exhibits an oxidation potential at 0.62 V vs Ag/AgCl which gives a reduction potential of −2.27 V vs Fc for **3a**. Considering that Fc has a HOMO value of −4.8 eV,[28] the LUMO value of **3a** is −2.53 eV (=−4.8 + 2.27). The triazines **3a**−**e** possess lower LUMO values (−2.53 to −2.72 eV) in comparison with 3,5-diphenyl-1,2,4-oxadiazole, which


Device (I)

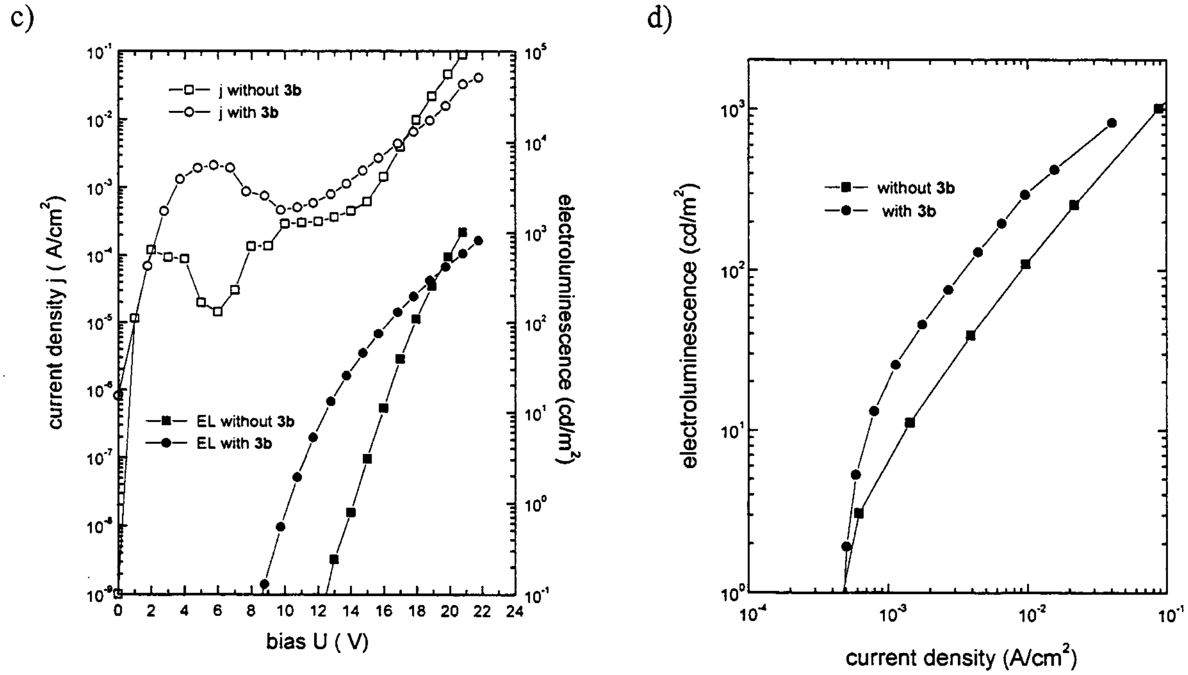

Device (II)

Figure 3. Comparison of LED characteristics both with and without **3b** of two different devices. (I): ITO/blend of PVK + TDAPB + Alq$_3$ (4:1:1)/Mg:Ag (10:1). (a) Current–voltage and luminance–voltage curves. (b) Efficiency plot of luminance against current density. (II): ITO/TDAPB/Alq$_3$/Mg:Ag(10:1). (c) Current–voltage and luminance–voltage curves. (d) Efficiency plot of luminance against current density.

shows a reversible reduction at −2.09 V vs Ag/AgCl corresponding to a LUMO value of −2.26 eV. The decrease of LUMO values for the triazine dimers implies that these compounds are favorable for electron injection.

LED Devices. The influence of the dimeric aromatic triazine ethers **3a**–**e** as an additional HBETL on device performance in organic LEDs was investigated and the results with **3b** as an example are presented here. The compound **3b** was applied as HBETL by vapor deposition (50 nm) in two different types of devices: (I) a polymer blend single layer device, ITO/blend of PVK + TDAPB + Alq$_3$ (4:1:1)/Mg:Ag (10:1) and (II) a multilayer device, ITO/TDAPB/Alq3/Mg:Ag (10:1). For device I, a blend of PVK, TDAPB, and Alq$_3$ (4:1:1) was spin coated onto an ITO (indium tin oxide, sheet resistance: 20 (Ω/□) substrate from 1% (wt/wt) solution in 1,2-dichloroethane to obtain 80 nm thick layer. For device II, pure TDAPB was first spin coated on ITO substrate from 2% (wt/wt) solution in cyclohexanone to get a layer of 40 nm thickness followed by vapor deposition of 60 nm thick Alq_3 layer on top of it. The devices with and without an additional layer of **3b** (50 nm) were finally subjected to cathode deposition by coevaporation of Mg and Ag at rates of 10:1 at a pressure $<10^{-5}$ mbar.

The EL spectra for both devices I and II are the same as the photoluminescence spetrum of Alq_3 exhibiting green emission. The influence of **3b** on the performance of an electroluminescent single layer device (I) is illustrated in Figure 3a and b. Current density−voltage and electroluminescence−voltage curves of the two-layer LEDs with **3b** exhibit a lower slope compared to the single-layer device without **3b**. The onset of the electroluminescence is increased by the use of a triazine layer. However, the efficiency of the two-layer LED is twice as that of the single-layer device (Figure 3b). Figure 3c compares the current density−voltage and the electroluminescence−voltage characteristics of the multilayer device II with and without an additional triazine ether layer. The current flow in the three-layer device, ITO/TDAPB/Alq_3/**3b**/Mg:Ag (10:1) is higher than that in the two-layer device, ITO/TDAPB/Alq_3/Mg:Ag (10:1) for voltages below 17 V. However, the EL intensity in the former device is comparatively higher compared to that in the latter despite an increase in total thickness of the device. Additionally, the onset voltage for the device with **3b** is considerably lower than that for the device without **3b** unlike in device I. The efficiencies of the devices are qualitatively compared by plotting luminance against current density in Figure 3d. It can be clearly seen that the efficiency was improved by a factor of 3 by using an additional **3b** layer in device II. Thus, an additional layer of 1,3,5-triazine dimer **3b** increases the efficiency of both single- and two-layer electroluminescent devices I and II. This is in close agreement with our own results regarding increase of efficiency using poly(triazine ether)s as HBETL in PPV-based LEDs[24] and also with the observation of Strukelj et al.,[17] Friend et al.,[19] and Kido et al.[39] regarding increase of efficiency using additional HBETL in various types of LEDs. The stability and durability of these devices can be examined only if these devices are encapsulated in an inert atmosphere against degradation. However, all devices presented here are not encapsulated and therefore the correlation between the amorphous/crystalline nature of the triazine dimers and the durability of the devices cannot be further elucidated by these experiments. Regardless, the applicability of the dimeric triazine ethers as HBETL in organic LEDs was clearly demonstrated with **3b** as an example. A detailed comparison of devices with regard to the durability by using various triazine dimers in organic LEDs will be presented elsewhere after the devices can be encapsulated in an inert atmosphere.

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