Asymmetric Triaryldiamines as Thermally Stable Hole Transporting Layers for Organic Light-Emitting Devices

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The synthesis of a series of asymmetric triaryldiamines has provided a number of materials with a wide range of thermal, electrochemical, and spectroscopic properties. The asymmetric materials described herein have two different diarylamine groups bound to a 1,4-phenylene or 4,4′-biphenylene core, i.e., $Ar_1Ar_2N-C_6H_4-NAr_1'Ar_3$ or Ar_1Ar_2N-biphenyl-$NAr_1'Ar_3$, respectively. The diarylamines studied include diphenylamine, phenyl-*m*-tolylamine, naphthylphenylamine, iminostilbene, iminodibenzyl, and carbazole. These materials were prepared by copper- and palladium-catalyzed coupling of aryl halides and diarylamines. The asymmetry inherent in these compounds prevents these low molecular mass compounds from crystallizing, thus yielding higher thermal stability over that of the symmetric derivatives. In all cases, the asymmetric diamines form stable glasses, with glass transition temperatures up to 125 °C. HOMO levels for these materials, estimated by cyclic voltammetry, show a broad range of values, with oxidation potentials both lower and higher than those of common hole transport materials used in organic light emitting devices.

Introduction

Organic light emitting devices (OLEDs) have attracted a great deal of attention due to their potential use in a wide range of lighting as well as high- and low-resolution display applications. The first efficient organic light emitting device was fabricated as a single heterostructure device, using vacuum-deposited molecular thin films.[1] This OLED consisted of a structure constructed on an ITO (indium tin oxide) anode, with a tertiary amine hole transporting layer (HTL), an aluminum coordination complex electron-transporting layer (ETL), and the device was capped with a Mg−Ag cathode. A schematic diagram of this single heterostructure OLED along with the materials used to build the OLED is shown in Figure 1. A number of other materials and structures have been reported for OLEDs, but the basic mechanism for electroluminescence (EL) in most OLEDs is very similar. When a potential is applied across the OLED, holes are injected from the anode into the HTL and migrate in the presence of the electric field to the HTL/ETL interface. The applied potential also leads to injection of electrons from the cathode into the ETL and subsequent migration of these carriers to the ETL/HTL interface. The materials used for the transport layers are chosen carefully so that

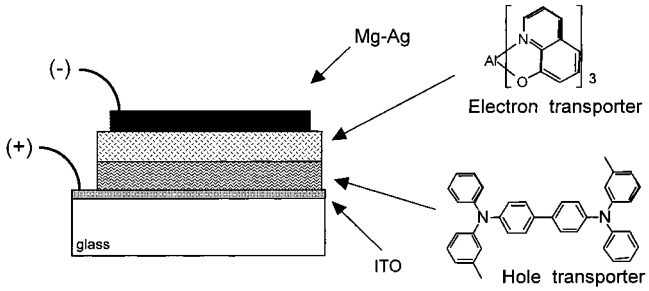

Figure 1. A schematic diagram of a single heterostructure OLED along with the structures of common materials used in OLEDs.

holes and electrons are preferentially conducted, but these materials do not conduct the opposite carrier to an appreciable extent. Thus, the HTL is both a hole conductor and an electron blocker and the ETL is both an electron conductor and a hole blocker. The proper choice of materials leads to a structure that confines the carriers in the organic materials and directs them to the HTL/ETL interface. Ideally, the holes and electrons recombine at or near the HTL/ETL interface to give excited molecules, or excitons, which radiatively relax to give the EL emission. The site of relaxation dictates the color of the EL emission, which can range from blue through the visible to the near-infrared depending on what materials are used to construct the OLED.[2]

One of the principal failure modes in OLEDs involves thermal instability in the molecular thin films. There are a number of sources of thermal stress on the OLEDs. In the fabrication of the OLED, deposition of the metal cathode heats the organic heterostructure. During OLED operation, both joule heating, due to the insulating nature of the organic materials,[3,4] and inefficient energy transfer in the devices contribute to the thermal

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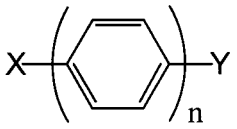
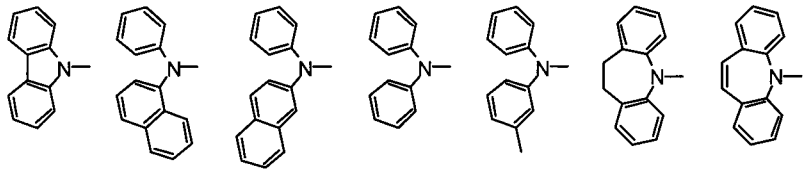
Chart 1





C **N_α** **N_β** **D** **T** **B** **S**

Abbreviation	X	Y	n	Abbreviation	X	Y	n
TPD (TTB)*	T	T	2	$SN_\alpha B$	S	N_α	2
NPD ($N_\alpha N_\alpha B$)*	N_α	N_α	2	$SN_\beta B$	S	N_β	2
CCB	C	C	2	SDB	S	D	2
DDP	D	D	1	STB	S	T	2
$N_\alpha N_\alpha P$	N_α	N_α	1	SBB	S	B	2
CCP	C	C	1	SSB	S	S	2
BCB	B	C	2	$BN_\alpha B$	B	N_α	2
SCB	S	C	2	BBB	B	B	2
$N_\alpha CP$	N_α	C	1	$N_\alpha CB$	N_α	C	2
TCP	T	C	1	SCP	S	C	1

* Abbreviations in parentheses are the systematic names based on the definitions in this paper. They are referred to in the text, however, by their common abbreviations, also listed above.

stress on the OLED. If an OLED is heated above the glass transition temperature of one of the organic materials in the device, irreversible failure is observed. One model suggests that the failure may be related to significant expansion of the material that is observed at its T_g,[5] leading to significant disruption of the multilayer structure. In addition to irreversible degradation occurring above the T_g, it has been proposed that poor device lifetimes observed for devices operated near room temperature are partly due to thermal instabilities of the amorphous organic layers.[6−8,176−8] The source of instability in these room temperature studies is thought to be dewetting and crystallization of the HTL materials, which occurs most readily in materials with comparatively low T_gs. In most OLED structures the HTL is the component with the lowest thermal stability. For example, the T_g for aluminum tris(8-hydroxyquinoline) (Alq), a common ETL, is 175 °C,[9] while those for TPD and NPD (see Chart 1), common HTLs, are reported to be 65 and 95 °C, respectively.[9]

A considerable amount of research has focused on developing new materials for hole-transporting layers in OLEDs.[9−20] Several requirements must be fulfilled for these materials to be viable in their use as HTLs. The material must have a low barrier to hole injection from the anode, have a high hole mobility, a low barrier to hole injection into the ETL or emissive layer, and be thermally stable in an amorphous or glassy state. While it is easy to list the properties that a given material must have to be a useful HTL, it is not typically the case that all of these parameters are known for a given material before it is used in an OLED. The materials

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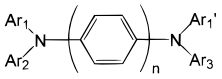
that have been found to have the best general match to the HTL requirements are triarylamines. These materials were well-known as hole conductors in xerographic applications long before they were used for OLEDs.[21] One of the most widely used HTL materials in OLEDs is TPD (4,4′-bis(phenyl-*m*-tolylamino)biphenyl). TPD fulfills the first four requirements for an HTL, giving devices with excellent EL efficiencies and low turn-on voltages;[22] however, the thermal stability is poor (T_g = 65 °C). In addition, although films of TPD are amorphous when deposited, they have been shown to crystallize in air at room temperature and at elevated temperatures (60−80 °C) in the absence of air.[10] This crystallization contributes to device failure.

The main objective for developing new HTL materials is to improve the thermal properties while maintaining the desired properties exhibited by TPD. A wide variety of approaches has been used in the endeavor to fulfill these requirements. For example, "starburst" molecules having a triphenylamine core have demonstrated improved thermal stability.[10,13,15,16] The addition of bulky groups to the phenyl rings of benzidine derivatives has yielded higher T_g materials as well as improved device lifetimes (e.g., NPD has a T_g of 95 °C).[11,17,20] Another approach involves the use of spiro linkages between traditional HTL materials, which uniformly increases T_g values.[23] A series of molecules with a thiophene bridge has exhibited reasonable thermal properties as an HTL as well as acting as a yellow emitter in devices.[12,14] The incorporation of TPD into a polymer, such as polymethacrylamide, has also been shown to improve thermal stability.[18] In most of these higher T_g HTL materials, the triarylamine is asymmetrically substituted; i.e., the amine nitrogen is bound to three different aryl groups. Asymmetric substitution of the triarylamine hinders crystallization, often leading to stable glasses. A simple example of this can be seen by comparing *N*,*N*,*N*′,*N*′-tetraphenylphenylenediamine (DDP in Chart 1) with the naphthyl-substituted derivative ($N_\alpha N_\alpha P$ in Chart 1). DDP does not form a glass, but gives exclusively a crystalline material with a melting point of 290 °C, while replacing one of the phenyl groups with a naphthyl group (forming $N_\alpha N_\alpha P$) gives a stable glass with a T_g of 68 °C and a melting point of 182 °C.

The study reported herein is aimed at improving the thermal and electronic properties of HTLs. We have prepared a large series of compounds with different triarylamines in order to probe how the thermal, oxidation, and electronic properties change by varying substituents. In this series, we have investigated a novel and systematic approach to increasing the T_g values of triarylamines. Some of the most efficient HTL materials are benzidine derivatives (4,4′-diaminobiphenyls), e.g., TPD and NPD. These materials are asymmetric in that they have three different aryl groups bound to each nitrogen atom (e.g., phenyl, naphthyl, and biphenyl for NPD), but the two nitrogen atoms are identically substituted. Our approach was to not only have materials with three different aryl groups on each nitrogen but to have asymmetry in the amines on either side of the biphenyl group; e.g., see Chart 2, Ar_1 Ar_2 Ar_3, Ar_1 may or may not be the same as Ar_1'. This asymmetry gives materials of this type a high propensity for forming stable glasses. It is important to point out, however, that the goal is to increase the glass transition temperature of the materials by making the molecules structurally asymmetric, without creating significant electronic asymmetry in the molecule. Electronic asymmetry, resulting in significant ground-state dipole moments for the molecules, would be expected to act as local carrier traps.[24] In addition to describing the thermal properties of these materials, we will discuss the oxidation potentials and electronic spectra of these asymmetric diamines.

Chart 2



Synthesis

General Methods. All amines, aryl halides, Cu, K_2CO_3, tris(dibenzylidineacetone)dipalladium (Pd_2dba_3), sodium *tert*-butoxide, diphenylphosphinoferrrocene (dppf), and 18-crown-6 were used as purchased from Aldrich without further purification. Sodium *tert*-butoxide, Pd_2dba_3, and dppf were stored and handled in a glovebox under nitrogen. Anhydrous toluene was purchased from Aldrich in Sure-Seal bottles or prepared by distilling reagent-grade toluene over sodium benzophenone.

Mass spectra were recorded on an HP 5973 mass spectrometer, using electron ionization at 70 eV. NMR spectra were measured on a Bruker AC 250 MHz spectrometer. The glass transition temperatures and melting points were measured using a TA Instruments 910 differential scanning calorimeter (DSC). The samples were heated at a rate of 20 °C per minute and were cooled using the quench cooling accessory provided with the instrument. UV spectra were measured with ∼10 μM solutions of each diamine with an AVIV 14DS UV spectrometer. Fluorescence studies were carried out on the same solutions of each diamine with a Photon Technology International fluorescence spectrometer. Lifetimes of each of the iminostilbene biphenyl derivatives were measured on degassed solutions using a PTI Timemaster lifetime system. Elemental analysis was provided by Atlantic Microlabs.

Elemental analyses were performed on several representative samples because of the numerous compounds with similar structures that were prepared. These were found, in general, to be slightly low in carbon content, likely due to carbonizing of the organics at the high temperatures required for the analysis of these thermally stable materials. Low-resolution MS and ^{1}H NMR confirm the identity and purity of the compounds. Many peaks in the NMR spectra exhibit nonfirst order coupling patterns due to the large number of aromatic protons with similar chemical shifts, and thus, the term multiplets (m) was often used. The number of peaks found on a given multiplet average well above 10. Coupling constants were measured and reported only when the multiplicity could be unambiguously determined.

Method 1. Palladium-Catalyzed Synthesis. The following reactions were carried out via procedures similar to those found in the literature.[25]

Singly Substituted Phenyl and Biphenyl Halide Synthesis. A round-bottomed flask was charged with Pd_2dba_3 (0.015 equiv), dppf (0.0225 equiv), and NaO^{t}Bu (1.5 equiv) in

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a nitrogen glovebox. Anhydrous toluene was added, and the reaction was stirred for 15 min. The 1,4-dibromobenzene or 4,4′-dibromobiphenyl (3−5 equiv) was added against a stream of nitrogen and the reaction was stirred for another 15 min. The mixture was heated to reflux for 8−24 h following the addition of the diarylamine (1.0 equiv). The reaction progress was followed by TLC (hexane or hexane/ethyl acetate) and/or MS until the diarylamine could not be detected.

Asymmetric Triaryldiamine Synthesis. The same synthesis was employed to prepare the asymmetric triaryldiamines, except 1.0 equiv of the aryl bromide and 1.1 equiv of the diarylamine were used. The reaction progress was monitored by the loss of the aryl bromide.

Symmetric Triaryldiamine Synthesis. The same synthesis was employed to prepare the symmetric triaryldiamines except the amounts of the reagents were used: Pd_2dba_3 (0.030 equiv), dppf (0.045 equiv), NaO^{t}Bu (3.0 equiv), 1,4-dibromobenzene or 4−4′-dibromobiphenyl (1.0 equiv), and diarylamine (2.1 equiv). The reaction progress was monitored by the loss of the diarylamine.

Purification. The reaction mixture was concentrated to dryness under reduced pressure, dissolved in minimal $CHCl_3$, and recrystallized with ethanol or hexanes. Very high purity products were required for our analyses and device fabrication. Therefore, all products were gradient sublimed, yielding in most cases a >99% pure product (as determined by MS and NMR). While the sublimation step increases the purity of the material significantly, the losses in sublimation decrease the yield by roughly 10−50%. It should be mentioned that it has since been found that the product could be also obtained by the sublimation of the crude reaction mixture in the absence of the recrystallization step with no noticeable loss of purity or yield. In the case of the singly substituted triarylamines, the excess 1,4-dibromobenzene or 4,4′-dibromobiphenyl was initially removed by sublimation at a lower temperature.

Method 2. Copper-Catalyzed Synthesis. The copper catalyzed reactions followed general Ullmann syntheses.[26]

Singly Substituted Phenyl and Biphenyl Halide Synthesis. A round-bottomed flask was charged with Cu (1.0 equiv), 18-crown-6 (0.15 equiv), and K_2CO_3 (2 equiv). *o*-Dichlorobenzene, 1,4-diiodobenzene (or 4,4′-diiodobiphenyl) (3−5 equiv), and the diarylamine (1.0 equiv) were added against a stream of nitrogen. The mixture was heated to 180−200 °C for 16−48 h. Reaction progress was followed until the diarylamine could not be detected. At the end of the reaction, the mixture was filtered hot through silica. The *o*-dichlorobenzene was then removed in vacuo, and the crude product was purified as previously mentioned.

Asymmetric Triaryldiamine Synthesis. The same synthesis was employed to prepare the asymmetric triaryldiamines except 1.0 equiv of the aryl bromide and 1.1 equiv of the diarylamine were used. The reaction progress was monitored by the loss of the aryl iodide.

Symmetric Triaryldiamine Synthesis. The same synthesis was employed to prepare the symmetric triaryldiamines except the following amounts of the reagents were used: Cu (2.0 equiv), 18-crown-6 (0.15 equiv), K_2CO_3 (4.0 equiv) 1,4-diiodobenzene or 4−4′-diiodobiphenyl (1.0 equiv), and diarylamine (2.0 equiv). The reaction progress was monitored by the loss of the diarylamine.

Singly Substituted Phenyl Halides. *N*-(4-Bromophenyl)carbazole (BrCP). BrCP was synthesized from 1,4-dibromobenzene and carbazole using method 1, yielding ∼65 g (70%): ^{1}H NMR (acetone-d_6) δ 8.24 (d, 2H, J = 7.7 Hz), 7.85 (d, 2H, J = 8.5 Hz), 7.60 (d, 2H, J = 8.5 Hz), 7.48−7.24 (m, 6H); GCMS m/z 323 (M$^+$, 100), 321 (M$^+$, 100), 241 (50), 121 (25).

***N*-(4-Bromophenyl)-1-naphthylphenylamine (BrN$_\alpha$P).** BrN$_\alpha$P was synthesized from 1,4-dibromobenzene and 1-naphthylphenylamine using method 1, yielding 1.9 g (59%): ^{1}H NMR ($CDCl_3$) δ 7.91 (d, 1H, J = 8.5 Hz), 7.81 (d, 1H, J = 8.3 Hz), 7.55−6.93 (m, ca. 12H), 6.88 (d, 2H, J = 9.3 Hz); MS m/z 375 (M$^+$, 100), 373 (M$^+$, 100), 293 (34), 216 (56), 127 (17), 77 (30).

***N*-(4-Bromophenyl)-2-naphthylphenylamine (BrN$_\beta$P).** BrN$_\beta$P was synthesized from 1,4-dibromobenzene and 2-naphthylphenylamine using method 1, yielding 1.9 g (59%): ^{1}H NMR ($CDCl_3$) δ 7.73 (t, 2H, J = 8.5 Hz), 7.58 (d, 1H, J = 7.8 Hz), 7.47−6.93 (m, ca. 13H); MS m/z 375 (M$^+$, 97), 373 (M$^+$, 97), 293 (40), 216 (100), 184 (46), 127 (36), 77 (93).

***N*-(4-Iodophenyl)diphenylamine (IDP).** IDP was synthesized from 1,4-diiodobenzene and diphenylamine using method 2, yielding 2.9 g (35%): ^{1}H NMR ($CDCl_3$) δ 7.34−6.87 (m, ca. 14H); MS m/z 371 (M$^+$, 100), 243 (39), 167 (58), 166 (70), 77 (78).

***N*-(4-Bromophenyl)phenyl-*m*-tolylamine (BrTP).** BrTP was synthesized from *p*-bromoiodobenzene and 3-methyldiphenylamine using method 2, yielding 2.6 g (30%): ^{1}H NMR ($CDCl_3$) δ 7.34−6.79 (m, ca. 13H), 2.24 (s, 3H); MS m/z 385 (M$^+$, 59), 339 (100), 337 (100), 257 (75), 180 (66), 152 (31), 128 (47), 77 (60).

***N*-(4-Bromophenyl)iminostilbene (BrSP).** BrSP was synthesized from 1,4-dibromobenzene and iminostilbene using method 1, yielding 2.2 g (40%): ^{1}H NMR ($CDCl_3$) δ 7.58−7.28 (m, ca. 9H), 7.03 (d, 2H, J = 9.3 Hz), 6.80 (s, 1H), 6.10 (d, 2H, J = 8.5 Hz); MS m/z 349 (M$^+$, 100), 347 (M$^+$, 100), 267 (63), 192 (77), 178 (77), 134 (68).

Singly Substituted Biphenyl Halides. 4-Iodo-4-(carbazolyl)biphenyl (ICB). ICB was synthesized from 4,4′-diiodobiphenyl and carbazole using method 2, yielding about 6.4 g (64%): ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 2H, J = 8.3 Hz), 7.82 (d, 2H, J = 8.5 Hz), 7.77 (d, 2H, J = 8.5 Hz), 7.63 (d, 2H, J = 8.5 Hz), 7.50−7.24 (m, 8H); MS m/z 445 (M$^+$, 68), 318 (70), 241 (12), 166 (50), 152 (100).

4-Iodo-4′-(1-naphthylphenylamino)biphenyl (IN$_\alpha$B). IN$_\alpha$B was synthesized from 4,4′-diiodobiphenyl and 1-naphthylphenylamine using method 2, yielding about 4.9 g (42%): ^{1}H NMR ($CDCl_3$) δ 7.92 (d, 1H, J = 8.3 Hz), 7.88 (d, 1H, J = 9.0 Hz), 7.78 (d, 1H, J = 7.5 Hz), 7.68 (d, 2H, J = 8.5 Hz), 7.53−6.90 (m, ca. 15H); MS m/z 497 (M$^+$, 31), 370 (9), 293 (17), 241 (18), 217 (40), 152 (30), 127 (32), 77 (100).

4-Iodo-4′-(2-naphthylphenylamino)biphenyl (IN$_\beta$B). IN$_\beta$B was synthesized from 4,4′-diiodobiphenyl and 2-naphthylphenylamine using method 2, yielding about 5.9 g (50%): ^{1}H NMR ($CDCl_3$) δ 7.73 (t, 4H, J = 8.3 Hz), 7.58 (d, 2H, J = 8.3 Hz), 7.47−6.94 (m, ca. 14H); MS m/z 497 (M$^+$, 100), 370 (68), 293 (62), 241 (48), 217 (83), 152 (57), 127 (40), 77 (72).

4-Iodo-4′-diphenylaminobiphenyl (IDB). IDB was synthesized from 4,4′-diiodobiphenyl and diphenylamine using method 2, yielding ∼5.7 g (54%): ^{1}H NMR ($CDCl_3$) δ 7.44−7.19 (m, ca. 14H); MS m/z 447 (M$^+$, 100), 320 (16), 241 (19), 167 (15), 77 (21).

4-Iodo-4′-(phenyl-*m*-tolylamino)biphenyl (ITB). ITB was synthesized from 4,4′-diiodobiphenyl and 3-methyldiphenylamine using method 2, yielding about 2.0 g (46%): ^{1}H NMR ($CDCl_3$) δ 7.73 (d, 2H, J = 8.8 Hz), 7.41 (d, 2H, J = 8.5 Hz), 7.34−6.83 (m, ca. 13H), 2.27 (s, 3H); MS m/z 461 (M$^+$, 2), 335 (100), 293 (10), 243 (10), 167 (12), 150 (20).

4-Iodo-4′-(iminodibenzyl)biphenyl (IBB). IBB was synthesized from 4,4′-diiodobiphenyl and iminodibenzyl using method 2, yielding ∼2.2 g (40%): ^{1}H NMR ($CDCl_3$) δ 7.66 (d, 2H, J = 8.3 Hz), 7.46−7.16 (m, ca. 12H), 6.63 (dd, 2H, J = 8.6, 3.0 Hz), 3.00 (s, 4H); MS m/z 473 (M$^+$, 22), 346 (16), 152 (100), 77 (42).

4-Bromo-4′-(iminostilbenyl)biphenyl (BrSB). ISB was synthesized from 4,4′-dibromobiphenyl and iminostilbene using method 1, yielding about 3.0 g (45%): ^{1}H NMR ($CDCl_3$) δ 7.52−7.15 (m, ca. 14H), 6.83 (s, 2H), 6.32 (d, 2H, J = 9.0 Hz); MS m/z 425 (M$^+$, 100), 423 (M$^+$, 100), 345 (34), 191 (47), 177 (28), 152 (40).

Asymmetric Phenyls. 1-Carbazolyl-4-(1-naphthylphenylamino)benzene (N$_\alpha$CP). N$_\alpha$CP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and 1-naphthylphenylamine using method 1, yielding 0.72 g (50%): ^{1}H NMR (acetone-d_6) δ 8.18 (d, 2H, J = 7.5 Hz), 8.10−7.99 (m, 2H), 7.94 (d, 2H, J = 7.5 Hz), 7.67−7.12 (m, ca. 18H), 7.02 (t, 1H, J = 8.3 Hz);

(26) Gauthier, S.; Frechet, J. M. J. *Synthesis* **1987**, 383.

MS *m/z* 460 (M^+, 100), 293 (30), 242 (13), 230 (M^{2+}, 57), 216 (26), 191 (12), 166 (21), 77 (6); abs λ_{max} = 320, 350 nm; E_{mm} λ_{max} = 416 nm.

1-Carbazolyl-4-(2-naphthylphenylamino)benzene (N_βCP). N_βCP was synthesized from *N*-(4-bromophenyl)-carbazole (BrCP) and 2-naphthylphenylamine using method 1, yielding 1.02 g (71%): ^{1}H NMR (acetone-d_6) δ 8.20 (d, 2H, J = 7.5 Hz), 7.87 (t, 2H, J = 8.3 Hz), 7.73 (d, 2H, J = 8.3 Hz), 7.63−7.18 (m, ca. 17H), 7.10 (t, 1H, J = 7.5 Hz); MS *m/z* 460 (M^+, 100), 293 (8), 242 (3), 230 (M^{2+}, 15), 216 (5), 166 (3), 77 (2); abs λ_{max} = 285, 295, 320 nm; E_{mm} λ_{max} = 409 nm.

1-Carbazolyl-4-(diphenylamino)benzene (DCP). DCP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and diphenylamine using method 1, yielding 0.54 g (42%): ^{1}H NMR (acetone-d_6) δ 8.20 (d, 2H, J = 7.5 Hz), 7.53−7.05 (m, ca. 20H); MS *m/z* 410 (M^+, 100), 243 (9), 241 (8), 205 (M^{2+}, 17), 166 (9), 77 (3); abs λ_{max} = 295, 320 nm; E_{mm} λ_{max} = 400 nm.

1-Carbazolyl-4-(phenyl-*m*-tolylamino)benzene (TCP). TCP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and 3-methyldiphenylamine using method 1, yielding 0.83 g (63%): ^{1}H NMR (acetone-d_6) δ 8.13 (d, 2H, J = 7.5 Hz), 7.47−7.15 (m, ca. 15H), 6.89 (d, 1H, J = 7.8 Hz), 2.30 (s, 3H); MS *m/z* 424 (M^+, 100), 258 (6), 241 (6), 212 (M^{2+}, 13), 181 (3), 166 (6); abs λ_{max} = 295, 315 nm; E_{mm} λ_{max} = 370 nm.

1-Carbazolyl-4-(iminodibenzyl)benzene (BCP). BCP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and iminodibenzyl using method 1, yielding 0.96 g (71%): ^{1}H NMR (acetone-d_6) δ 8.17 (d, 2H, J = 7.8 Hz), 7.52 (d, 2H, J = 7.0 Hz), 7.48−7.16 (m, ca. 14H), 6.76 (d, 2H, J = 9.2 Hz), 3.08 (s, 4H); MS *m/z* 436 (M^+, 100), 268 (5), 241 (7), 218 (13), 194 (10), 166 (3); abs λ_{max} = 295 nm; E_{mm} λ_{max} = 382 nm.

1-Carbazole-4-(iminostilbenyl)benzene (SCP). SCP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and iminostilbene using method 1, yielding 0.75 g (56%): ^{1}H NMR (acetone-d_6) δ 8.14 (d, 2H, J = 7.5 Hz), 7.69−7.13 (m, ca. 16H), 6.99 (s, 2H), 6.44 (d, 2H, J = 9.2 Hz); MS *m/z* 434 (M^+, 100), 268 (7), 255 (10), 242 (5), 217 (M^{2+}, 15), 192 (5), 165 (4); Abs λ_{max} = 270, 300 nmp; E_{mm} λ_{max} = 393, 487 nm. Anal. Calcd for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10; N, 6.45. Found: C, 87.53; H, 5.74; N, 6.32.

1-(1-Naphthylphenylamino)-4-(2-naphthylphenylamino)benzene ($N_\beta N_\alpha$P). $N_\beta N_\alpha$P was synthesized from *N*-(4-bromophenyl)-1-naphthylphenylamine (BrN_αP) and 2-naphthylphenylamine using method 1, yielding 0.43 g (63%): ^{1}H NMR ($CDCl_3$) δ 7.96 (d, 1H, J = 8.3 Hz), 7.87 (d, 1H, J = 8.5 Hz), 7.81−6.83 (m, ca. 26H); MS *m/z* 512 (M^+, 100), 385 (2), 293 (23), 256 (M^{2+}, 51), 217 (59), 191 (12), 127 (11), 77 (13); Abs λ_{max} = 280, 320 nm; E_{mm} λ_{max} = 399, 496 nm.

1-(1-Naphthylphenylamino)-4-(diphenylamino)benzene (DN_αP). DN_αP was synthesized from *N*-(4-bromophenyl)-1-naphthylphenylamine (BrN_αP) and diphenylamine using method 1, yielding 0.48 g (77%): ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 7.5 Hz), 7.74 (d, 1H, J = 8.5 Hz), 7.52−6.79 (m, ca. 23H); MS *m/z* 462 (M^+, 100), 293 (10), 242 (11), 217 (38), 167 (40), 127 (20), 77 (78); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 414, 501 nm.

1-(1-Naphthylphenylamino)-4-(phenyl-*m*-tolylamino)benzene (TN_αP). TN_αP was synthesized from *N*-(4-bromophenyl)-1-naphthylphenylamine (BrN_αP) and 3-methyldiphenylamine using method 1, yielding 0.37 g (58%): ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 1H, J = 8.5 Hz), 7.87 (d, 1H, J = 7.5 Hz), 7.75 (d, 1H, J = 8.5 Hz), 7.52−6.82 (m, ca. 21H), 6.77 (d, 1H, J = 7.8 Hz), 2.24 (s, 3H); MS *m/z* 476 (M^+, 100), 293 (21), 257 (14), 238 (M^{2+}, 60), 217 (50), 167 (43), 127 (11), 77 (22); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 417, 506 nm.

1-(1-Naphthylphenylamino)-4-(iminodibenzyl)benzene (BN_αP). BN_αP was synthesized from *N*-(4-bromophenyl)-1-naphthylphenylamine (BrN_αP) and iminodibenzyl using method 1, yielding 0.31 g (67%): ^{1}H NMR ($CDCl_3$) δ 7.93 (d, 1H, J = 7.8 Hz), 7.81 (d, 1H, J = 8.5 Hz), 7.67 (d, 1H, J = 7.5 Hz), 7.47−7.10 (m, ca. 15H), 6.90 (d, 2H, J = 8.5 Hz), 6.76 (d, 2H, J = 8.5 Hz), 6.45 (d, 2H, J = 8.8 Hz), 2.98 (s, 4H); MS *m/z* 488 (M^+, 100), 308 (4), 294 (16), 268 (16), 244 (M^{2+}, 55), 217 (21), 194 (23), 127 (6), 77 (8); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 398, 510 nm.

1-(1-Naphthylphenylamino)-4-(iminostilbenyl)benzene (SN_αP). SN_αP was synthesized from *N*-(4-bromophenyl)-iminostilbene(BrSP) and 1-naphthylphenylamine using method 1, yielding 0.44 g (63%): ^{1}H NMR ($CDCl_3$) δ 7.98 (d, 1H, J = 8.0 Hz), 7.90 (d, 1H, J = 7.5 Hz), 7.66 (d, 1H, J = 8.3 Hz), 7.59−6.65 (m, ca. 19H), 6.39 (d, 2H, J = 8.3 Hz), 6.19 (d, 2H, J = 8.8 Hz); MS *m/z* 486 (M^+, 100), 293 (3), 267 (3), 243 (M^{2+}, 27), 192 (17), 127 (3), 77 (7); Abs λ_{max} = 300, 350 nm; E_{mm} λ_{max} = 407 nm.

1-(2-Naphthylphenylamino)-4-(diphenylamino)benzene (DN_βP). DN_βP was synthesized from *N*-(4-bromophenyl)-2-naphthylphenylamine (BrPP) and diphenylamine using method 1, yielding 0.33 g (53%): ^{1}H NMR ($CDCl_3$) δ 7.71 (t, 2H, J = 9.2 Hz), 7.89 (d, 1H, J = 7.8 Hz), 7.44−6.93 (m, ca. 23H); MS *m/z* 462 (M^+, 100), 385 (3), 293 (30), 243 (14), 231 (M^{2+}, 56), 217 (15), 167 (50), 127 (15), 77 (38); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 399, 475 (sh) nm.

1-(2-Naphthylphenylamino)-4-(phenyl-*m*-tolylamino)benzene (TN_βP). TN_βP was synthesized from *N*-(4-bromophenyl)-2-naphthylphenylamine (BrN_βP) and 2-methyldiphenylamine using method 1, yielding 0.46 g (73%): ^{1}H NMR ($CDCl_3$) δ 7.72 (t, 2H, J = 8.5 Hz), 7.59 (d, 1H, J = 7.5 Hz), 7.44−6.87 (m, ca. 21H), 6.82 (d, 1H, J = 7.5 Hz), 2.27 (s, 3H); MS *m/z* 476 (M^+, 100), 293 (28), 238 (M^{2+}, 58), 217 (56), 167 (55), 127 (13), 77 (23); abs λ_{max} = 320 nm; E_{mm} λ_{max} = 398, 470 nm.

1-(2-Naphthylphenylamino)-4-(iminodibenzyl)benzene (BN_βP). BN_βP was synthesized from *N*-(4-bromophenyl)-2-naphthylphenylamine (BrN_βP) and iminodibenzyl using method 1, yielding 0.27 g (60%): ^{1}H NMR ($CDCl_3$) δ 7.76−6.85 (m, ca. 23H), 6.53 (d, 1H, J = 8.5 Hz), 3.03 (s, 4H); MS *m/z* 488 (M^+, 100), 294 (10), 268 (10), 244 (M^{2+}, 36), 217 (20), 194 (23), 180 (13), 127 (8), 77 (9); Abs λ_{max} = 280, 320 nm; E_{mm} λ_{max} = 398, 475 nm.

1-(2-Naphthylphenylamino)-4-(iminostilbenyl)benzene (SN_βP). SN_βP was synthesized from *N*-(4-bromophenyl)-iminostilbene (BrN_βP) and 2-naphthylphenylamine using method 1, yielding 0.35 g (50%): ^{1}H NMR ($CDCl_3$) δ 7.76 (d, 1H, J = 7.5 Hz), 7.60 (d, 1H, J = 8.3 Hz), 7.55−6.82 (m, ca. 20H), 6.79 (d, 2H, J = 9.0 Hz), 6.22 (d, 2H, J = 9.0 Hz); MS *m/z* 486 (M^+, 100), 307 (5), 294 (4), 267 (4), 243 (M^{2+}, 14), 192 (14), 178 (4), 127 (4), 77 (4); Abs λ_{max} = 280, 315 nm; E_{mm} λ_{max} = 402 nm.

1-(Diphenylamino)-4-(phenyl-*m*-tolylamino)benzene (TDP). TDP was synthesized from *N*-(4-bromophenyl)phenyl-*m*-tolylamine (BrTP) and diphenylamine using method 1, yielding 0.35 g (59%): ^{1}H NMR ($CDCl_3$) δ 7.31−6.69 (m, ca. 23H), 2.25 (s, 3H); MS *m/z* 426 (M^+, 100), 257 (5), 243 (4), 213 (M^{2+}, 19), 166 (40), 77 (18); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 397 nm.

1-(Diphenylamino)-4-(iminodibenzyl)benzene (BDP). BDP was synthesized from *N*-(4-iodophenyl)diphenylamine (IDP) and iminodibenzyl using method 1, yielding 0.30 g (50%): ^{1}H NMR ($CDCl_3$) δ 7.34−6.65 (m, ca. 20H), 6.65 (d, 2H, J = 8.6 Hz), 3.03 (s, 4H); MS *m/z* 438 (M^+, 100), 360 (45), 219 (M^{2+}, 30).

1-(Diphenylamino)-4-(iminostilbenyl)benzene (SDP). SDP was synthesized from *N*-(4-bromophenyl)iminostilbene (BrDP) and diphenylamine using method 1, yielding 0.29 g (47%): ^{1}H NMR ($CDCl_3$) δ 7.51−6.70 (m, ca. 20H), 6.75 (d, 2H, J = 9.0 Hz), 6.20 (d, 2H, J = 8.3 Hz); MS *m/z* 436 (M^+, 100), 359 (5), 268 (13), 257 (21), 218 (M^{2+}, 27), 192 (22), 178 (12), 77 (13); Abs λ_{max} = 310 nm; E_{mm} λ_{max} = 398 nm.

1-(Phenyl-*m*-tolylamino)-4-(iminodibenzyl)benzene (BTP). BTP was synthesized from *N*-(4-bromophenyl)phenyl-*m*-tolylamine (BrTP) and iminodibenzyl using method 1, yielding 0.36 g (58%): ^{1}H NMR ($CDCl_3$) δ 7.41 (d, 2H, J = 8.0 Hz), 7.32−6.65 (m, ca. 17H), 6.49 (d, 2H, J = 8.4 Hz), 3.01 (s, 4H), 2.21 (s, 3H); MS *m/z* 452 (M^+, 38), 178 (100), 152 (37), 77 (92); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 398 nm.

1-(Phenyl-*m*-tolylamino)-4-(iminostilbenyl)benzene (STP). STP was synthesized from *N*-(4-bromophenyl)iminostilbene (BrTP) and 3-methyldiphenylamine using method 1, yielding 0.37 g (57%): ^{1}H NMR ($CDCl_3$) δ 7.55−6.80 (m, ca. 19H), 6.77 (d, 2H, J = 9.0 Hz), 6.19 (d, 2H, J = 9.0 Hz), 2.19

(s, 3H); MS *m*/*z* 450 (M^+, 100), 271 (9), 257 (9), 225 (M^{2+}, 9), 192 (26), 178 (20), 165 (21), 77 (16); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 400 nm.

1-(Iminodibenzyl)-4-(iminostilbenyl)benzene (SBP). SBP was synthesized from *N*-(4-bromophenyl)iminostilbene (BrSP) and iminodibenzyl using method 1, yielding 0.38 g (57%): ^{1}H NMR ($CDCl_3$) δ 7.48−7.04 (m, ca. 16H), 6.78 (s, 2H), 6.33 (d, 2H, J = 9.0 Hz), 6.08 (d, 2H, J = 8.3 Hz), 2.93 (s, 4H); MS *m*/*z* 462 (M^+, 100), 284 (15), 268 (33), 231 (M^{2+}, 60), 192 (52), 178 (39), 165 (32); Abs λ_{max} = 310 nm; E_{mm} λ_{max} = 395 nm. Anal. Calcd for $C_{34}H_{26}N_2$: C, 88.28; H, 5.67; N, 6.06. Found: C, 87.13; H, 5.57; N, 5.94.

Asymmetric Biphenyls. 4-Carbazolyl-4′-(1-naphthylphenylamino)biphenyl (N_αCB). N_αCB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and 1-naphthylphenylamine using method 1, yielding 0.37 g (54%): ^{1}H NMR ($CDCl_3$) δ 8.21−6.92 (m, ca. 28H); MS *m*/*z* 536 (M^+, 38), 342 (10), 240 (50), 216 (100), 165 (46), 126 (40), 76 (50); Abs λ_{max} = 295, 320 nm; E_{mm} λ_{max} = 422 nm.

4-Carbazolyl-4′-(2-naphthylphenylamino)biphenyl (N_βCB). N_βCB was synthesized from 4-bromo-4′-(carbazolyl)-biphenyl (BrCB) and 2-naphthylphenylamine using method 1, yielding 0.41 g (61%): ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 2H, J = 7.5 Hz), 7.82−7.16 (m, ca. 24H), 7.08 (t, 2H, J = 6.8 Hz); MS *m*/*z* 536 (M^+, 100), 342 (8), 217 (62), 127 (32), 76 (25); Abs λ_{max} = 295, 320, 345 nm; E_{mm} λ_{max} = 404 nm.

4-Carbazolyl-4′-(diphenylamino)biphenyl (DCB). DCB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and diphenylamine using method 1, yielding 0.13 g (27%): ^{1}H NMR ($CDCl_3$) δ 8.22 (d, 2H, J = 7.0 Hz), 7.98 (d, 1H, J = 8.3 Hz), 7.91−7.18 (m, ca. 21H), 7.12 (t, 2H, J = 7.5 Hz); MS *m*/*z* 486 (M^+, 100), 408 (2), 319 (7), 243 (M^{2+}, 37), 166 (4), 77 (2); Abs λ_{max} = 295, 340 nm; E_{mm} λ_{max} = 390 nm.

4-Carbazolyl-4′-(phenyl-*m*-tolylamino)biphenyl (TCB). TCB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and 3-methyldiphenylamine using method 1, yielding 0.35 g (70%): ^{1}H NMR ($CDCl_3$) δ 8.15 (d, 2H, J = 7.5 Hz), 7.78 (d, 2H, J = 8.3 Hz), 7.59 (d, 2H, J = 8.3 Hz), 7.55 (d, 2H, J = 9.0 Hz), 7.50−6.91 (m, ca. 16H), 6.88 (d, 1H, J = 7.5 Hz), 2.28 (s, 3H); MS *m*/*z* 500 (M^+, 100), 333 (10), 318 (7), 250 (M^{2+}, 62), 166 (12); abs λ_{max} = 295, 345 nm; E_{mm} λ_{max} = 400 nm.

4-Carbazolyl-4′-(iminodibenzyl)biphenyl (BCB). BCB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and iminodibenzyl using method 1, yielding 0.27 g (56%): ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 2H, J = 7.5 Hz), 7.76−7.20 (m, ca. 20H), 6.70 (d, 2H, J = 8.5 Hz), 3.04 (s, 4H); MS *m*/*z* 512 (M^+, 100), 256 (M^{2+}, 19), 194 (11), 167 (5), 152 (6); abs λ_{max} = 295, 325 nm; E_{mm} λ_{max} = 373 nm. Anal. Calcd for $C_{40}H_{32}N_2$: C, 89.03; H, 5.51; N, 5.46. Found: C, 88.28; H, 5.36; N, 5.33.

4-Carbazolyl-4′-(iminostilbenyl)biphenyl (SCB). SCB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and iminostilbene using method 1, yielding 0.42 g (73%): ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 2H, J = 7.5 Hz), 7.72−7.22 (m, ca. 20H), 6.87 (s, 2H), 6.41 (d, 2H, J = 8.5 Hz); MS *m*/*z* 510 (M^+, 100), 343 (11), 332 (10), 315 (13), 255 (M^{2+}, 70), 192 (40), 178 (15), 166 (57), 152 (28), 139 (12); Abs λ_{max} = 295, 315 nm; E_{mm} λ_{max} = 386 nm. Anal. Calcd for $C_{38}H_{26}N_2$: C, 89.38; H, 5.13; N, 5.49. Found: C, 89.27; H, 5.07; N, 5.49.

4-(1-Naphthylphenylamino)-4′-(2-naphthylphenylamino)biphenyl ($N_\beta N_\alpha$B). PN_αB was synthesized from 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN_αB) and 2-naphthylphenylamine using method 2, yielding 0.45 g (38%): ^{1}H NMR ($CDCl_3$) δ 7.94 (d, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 7.8 Hz), 7.81−6.86 (m, ca. 30H); MS *m*/*z* 588 (M^+, 100), 369 (3), 294 (M^{2+}, 40), 217 (27), 77 (5); Abs λ_{max} = 340 nm; E_{mm} λ_{max} = 431 nm.

4-(1-Naphthylphenylamino)-4′-(diphenylamino)biphenyl (DN_αB). DN_αB was synthesized from 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN_αB) and diphenylamine using method 2, yielding 0.28 g (43%): ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 1H, J = 7.8 Hz), 7.88 (d, 1H, J = 7.8 Hz), 7.83−6.85 (m, ca. 28H); MS *m*/*z* 538 (M^+, 100), 369 (3), 269 (M^{2+}, 34), 217 (9), 167 (8), 77 (3); Abs λ_{max} = 310, 350 nm; E_{mm} λ_{max} = 400 (sh), 450 nm.

4-(1-Naphthylphenylamino)-4′-(phenyl-*m*-tolylamino)biphenyl (TN_αB). TN_αB was synthesized from 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN_αB) and 3-methyldiphenylamine using method 2, yielding 0.24 g (36%): ^{1}H NMR ($CDCl_3$) δ 7.93 (d, 1H, J = 7.8 Hz), 7.86 (d, 1H, J = 7.8 Hz), 7.81−6.75 (m, ca. 27H), 2.15 (s, 3H); MS *m*/*z* 552 (M^+, 100), 332 (1), 276 (M^{2+}, 25), 217 (7), 167 (5), 77 (3); Abs λ_{max} = 315, 350 nm; E_{mm} λ_{max} = 450 nm.

4-(1-Naphthylphenylamino)-4′-(iminodibenzyl)biphenyl (BN_αB). BN_αB was synthesized from 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN_αB) and iminodibenzyl using method 2, yielding 0.36 g (32%): ^{1}H NMR ($CDCl_3$) δ 7.96 (d, 1H, J = 7.6 Hz), 7.89 (d, 1H, J = 9.2 Hz), 7.82 (d, 1H, J = 8.4 Hz), 7.75 (d, 1H, J = 8.4 Hz), 7.55−6.82 (m, ca. 21H), 6.59 (d, 2H, J = 9.2 Hz), 2.99 (s, 4H); MS *m*/*z* 564 (M^+, 100), 369 (5), 344 (3), 282 (M^{2+}, 37), 217 (16), 194 (21), 77 (5). Anal. Calcd for $C_{42}H_{32}N_2$: C, 89.33; H, 5.71; N, 4.96. Found: C, 88.55; H, 5.37; N, 4.55.

4-(1-Naphthylphenylamino)-4′-(iminostilbenyl)biphenyl (SN_αB). SN_αB was synthesized from 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN_αB) and iminostilbene using method 1, yielding 0.23 g (79%): ^{1}H NMR ($CDCl_3$) δ 7.91 (d, 1H, J = 7.6 Hz), 7.85 (d, 1H, J = 8.4 Hz), 7.73 (d, 1H, J = 7.6 Hz), 7.53−6.79 (m, ca. 25H), 6.29 (d, 2H, J = 9.2 Hz); MS *m*/*z* 562 (M^+, 100), 281 (M^{2+}, 50), 217 (10), 192 (17), 165 (8); Abs λ_{max} = 270, 330 nm; E_{mm} λ_{max} = 404, 507(br) nm. Anal. Calcd for $C_{42}H_{30}N_2$: C, 89.65; H, 5.37; N, 4.98. Found: C, 87.95; H, 5.32; N, 4.82.

4-(2-Naphthylphenylamino)-4′-(diphenylamino)biphenyl (DN_βB). DN_βB was synthesized from 4-iodo-4′-(diphenylamino)biphenyl (IDB) and 2-naphthylphenylamine using method 2, yielding 0.37 g (31%): ^{1}H NMR ($CDCl_3$) δ 7.81 (t, 2H, J = 8.4 Hz), 7.67 (d, 1H, J = 7.6 Hz), 7.58−7.03 (m, ca. 27H); MS *m*/*z* 538 (M^+, 100), 369 (8), 269 (M^{2+}, 58), 217 (23), 167 (12), 77 (9); Abs λ_{max} = 320, 350 nm; E_{mm} λ_{max} = 417 nm.

4-(2-Naphthylphenylamino)-4′-(phenyl-*m*-tolylamino)biphenyl (TN_βB). TN_βB was synthesized from 4-iodo-4′-(2-naphthylphenylamino)biphenyl (IN_βB) and 3-methyldiphenylamine using method 2, yielding 0.49 g (44%): ^{1}H NMR ($CDCl_3$) δ 7.73 (t, 2H, J = 9.2 Hz), 7.59 (d, 1H, J = 8.4 Hz), 7.52−6.80 (m, ca. 26H), 2.26 (s, 3H); MS *m*/*z* 552 (M^+, 100), 369 (10), 276 (M^{2+}, 95), 216 (76), 166 (47), 77 (40); Abs λ_{max} = 320, 350 nm; E_{mm} λ_{max} = 415 nm.

4-(2-Naphthylphenylamino)-4′-(iminodibenzyl)biphenyl (BN_βB). BN_βB was synthesized from 4-iodo-4′-(iminodibenzyl)biphenyl (IBB) and 2-naphthylphenylamine using method 2, yielding 0.27 g (25%): ^{1}H NMR ($CDCl_3$) δ 7.71 (t, 2H, J = 9.2 Hz), 7.57 (d, 1H, J = 9.2), 7.47−6.94 (m, ca. 23H), 6.62 (d, 2H, J = 9.2 Hz), 3.00 (s, 4H); MS *m*/*z* 564 (M^+, 100), 368 (15), 296 (15), 282 (M^{2+}, 14), 217 (5), 77 (3); abs λ_{max} = 330 nm; E_{mm} λ_{max} = 414 nm.

4-(2-Naphthylphenylamino)-4′-(iminostilbenyl)biphenyl (SN_βB). SN_βB was synthesized from 4-iodo-4′-(2-naphthylphenylamino)biphenyl (IN_βB) and iminostilbene using method 1, yielding 0.37 g (73%): ^{1}H NMR ($CDCl_3$) δ 7.81−6.95 (m, ca. 26H), 6.83 (s, 2H), 6.33 (d, 2H, J = 8.4 Hz); MS *m*/*z* 562 (M^+, 100), 369 (3), 281 (M^{2+}, 32), 217 (13), 192 (18), 77 (3); Abs λ_{max} = 280, 330 nm; E_{mm} λ_{max} = 413, 518 (w,br) nm. Anal. Calcd for $C_{42}H_{30}N_2$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.54; H, 5.43; N, 4.87.

4-(Diphenylamino)-4′-(phenyl-*m*-tolylamino)biphenyl (TDB). TDB was synthesized from 4-iodo-4′-(diphenylamino)biphenyl (IDB) and 3-methyldiphenylamine using method 1, yielding 0.45 g (80%): ^{1}H NMR ($CDCl_3$) δ 7.48−6.80 (m, ca. 27H), .2.25 (s, 3H); MS *m*/*z* 502 (M^+, 100), 333 (8), 319 (7), 251 (M^{2+}, 68), 167 (15), 77 (8); Abs λ_{max} = 310, 350 nm; E_{mm} λ_{max} = 396 nm.

4-(Diphenylamino)-4′-(iminodibenzyl)biphenyl (BDB). BDB was synthesized from 4-iodo-4′-(diphenylamino)biphenyl (IDB) and iminodibenzyl using method 1, yielding 0.26 g (51%): ^{1}H NMR ($CDCl_3$) δ 7.46−6.93 (m, ca. 24H), 6.62 (d, 2H, J = 9.2 Hz), 3.00 (s, 4H); MS *m*/*z* 514 (M^+, 100), 257 (M^{2+}, 24), 194 (10), 167 (8), 77 (3); Abs λ_{max} = 340 nm; E_{mm} λ_{max} = 400 nm.

4-(Diphenylamino)-4′-(iminostilbenyl)biphenyl (SDB). SDB was synthesized from 4-bromo-4′-(iminostilbenyl)biphenyl (BrSB) and diphenylamine using method 1, yielding 0.64 g (53%): ^{1}H NMR ($CDCl_3$) δ 7.58−6.90 (m, ca. 24H), 6.83 (s, 2H), 6.31 (d, 2H, J = 8.4 Hz); MS m/z 512 (M^+, 100), 256 (M^{2+},17), 192 (20), 192 (20), 178 (18), 165 (16), 152 (8), 77 (10); Abs λ_{max} = 310 (sh), 330 nm; E_{mm} λ_{max} = 397, 513 (br) nm.

4-(Phenyl-*m*-tolylamino)-4′-(iminodibenzyl)biphenyl (BTB). BTB was synthesized from 4-iodo-4′-(iminodibenzyl)-biphenyl (IBB) and 3-methyldiphenylamine using method 2, yielding 0.28 g (25%): ^{1}H NMR ($CDCl_3$) δ 7.45−6.85 (m, ca. 22H), 6.80 (d, 1H, J = 8.4 Hz), 6.61 (d, 2H, J = 8.4), 2.99 (s, 4H), 2.23 (s, 3H); MS m/z 528 (M^+, 67), 348 (17), 194 (66), 179 (74), 178 (100), 151 (38), 77 (32); Abs λ_{max} = 340 nm; E_{mm} λ_{max} = 402 nm.

4-(Phenyl-*m*-tolylamino)-4′-(iminostilbenyl)biphenyl (STB). STB was synthesized from 4-iodo-4′-(iminostilbene)-biphenyl (ISB) and 3-methyldiphenylamine using method 1, yielding 0.55 g (44%): ^{1}H NMR ($CDCl_3$) δ 7.53−6.76 (m, ca. 25H), 6.31 (d, 2H, J = 9.2 Hz), 2.23 (s, 3H); MS m/z 526 (M^+, 100), 263 (M^{2+}, 9), 193 (28), 178 (29), 152 (10), 77 (8); Abs λ_{max} = 310 (sh), 340 nm; E_{mm} λ_{max} = 397, 517 nm.

4-(Iminodibenzyl)-4′-(iminostilbenyl)biphenyl (SBB). SBB was synthesized from 4-iodo-4′-(iminostilbenyl)biphenyl (ISB) and iminodibenzyl using method 1, yielding 0.30 g (48%): ^{1}H NMR ($CDCl_3$) δ 7.08−7.56 (m, ca. 20H), 6.82 (s, 2H), 6.57 (d, 2H, J = 8.4 Hz), 6.29 (d, 2H, J = 9.2 Hz), 2.98 (s, 4H); MS m/z 538 (M^+, 100), 344 (6), 269 (M^{2+}, 32), 194 (16), 192 (20), 178 (13), 165 (12); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 411, 533 (w,br) nm. Anal. Calcd for $C_{40}H_{30}N_2$: C, 89.19; H, 5.61; N, 5.20. Found: C, 88.14; H, 5.62; N, 5.10.

Symmetric Phenyls. 1,4-Bis(carbazolyl)benzene (CCP). CCP was synthesized from 1,4-dibromobenzene and carbazole using method 1, yielding 1.68 g (17%): ^{1}H NMR ($CDCl_3$) δ 8.18 (d, 4H, J = 7.9 Hz), 7.81 (s, 4H), 7.57 (d, 4H, J = 8.5 Hz), 7.47 (td, 4H, J = 7.3, 1.2 Hz), 7.33 (td, 4H, J = 7.3, 1.2 Hz); MS m/z 408 (M^+, 100), 241 (4), 204 (M^{2+}, 50), 166 (8), 140 (8); Abs λ_{max} = 295, 310 nm; E_{mm} λ_{max} = 343 nm.

1,4-Bis(1-naphthylphenylamino)benzene ($N_\alpha N_\alpha P$). $N_\alpha N_\alpha P$ was synthesized from 1,4-diiodobenzene and 1-naphthylphenylamine using method 2, yielding 15.3 g (26%): ^{1}H NMR (acetone-d_6) δ 7.96 (d, 2H, J = 9.2 Hz), 7.84 (d, 2H, J = 9.2 Hz), 7.58−7.31 (m, 8H), 7.22−7.11 (m, 6H), 6.96 (s, 4H), 6.93−6.80 (m, 4H); MS m/z 512 (M^+, 100), 293 (10), 256 (M^{2+}, 32), 217 (30); Abs λ_{max} = 280, 320 nm; E_{mm} λ_{max} = 505 nm.

1,4-Bis(2-naphthylphenylamino)benzene ($N_\beta N_\beta P$). $N_\beta N_\beta P$ was synthesized from 1,4-diiodobenzene and 2-naphthylphenylamine using method 2, yielding 2.15 g (52%): ^{1}H NMR (acetone-d_6) δ 7.81 (d, 4H, J = 8.8 Hz), 7.67 (d, 2H, J = 7.8 Hz), 7.48−7.25 (m, 12), 7.21−7.01 (m, 10H); MS m/z 512 (M^+, 100), 369 (5), 293 (15), 256 (M^{2+}, 13), 217 (39), 191 (8), 127 (7), 77 (7); Abs λ_{max} = 260, 280, 325 nm; E_{mm} λ_{max} = 471 nm.

1,4-Bis(diphenylamino)benzene (DDP). DDP was synthesized from 1,4-dibromobenzene and diphenylamine using method 1, yielding 0.58 g (31%): ^{1}H NMR ($CDCl_3$) δ 7.32−7.22 (m, 8H), 7.10−6.96 (m, 16H); MS m/z 412 (M^+, 100), 243 (9), 206 (M^{2+}, 9), 167 (44), 77 (30); Abs λ_{max} = nm; E_{mm} λ_{max} = nm.

1,4-Bis(phenyl-*m*-tolylamino)benzene (TTP). TTP was synthesized from 3-iodotoluene and N,N′-diphenyl-1,4-phenylenediamine using method 2, yielding 2.66 g (76%): ^{1}H NMR (acetone-d_6) δ 7.31−6.81 (m, 22H), 2.33 (s, 6H); MS m/z 440 (M^+, 100), 256 (10), 220 (M^{2+}, 26), 166 (32), 77 (8); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 376 nm.

1,4-Bis(iminodibenzyl)benzene (BBP). BBP was synthesized from 1,4-dibromobenzene and iminodibenzyl using method 1, yielding 0.55 g (11%): ^{1}H NMR ($CDCl_3$) δ 7.55−6.51 (m, 20H), 3.19 (s, 4H), 3.03 (s, 4H); MS m/z 464 (M^+, 100), 232 (M^{2+}, 17), 194 (16), 165 (10); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 368 nm.

1,4-Bis(iminostilbenyl)benzene (SSP). SSP was synthesized from 1,4-dibromobenzene and iminostilbene using method 1, yielding 1.3 g (47%): ^{1}H NMR ($CDCl_3$) δ 7.52−7.27 (m, 16H), 6.81 (s, 4H), 5.88 (s, 4H); MS m/z 460 (M^+, 100), 280 (10), 230 (M^{2+}, 13), 192 (11), 165 (8); Abs λ_{max} = 290, 340 nm; E_{mm} λ_{max} = 444, 488 nm.

Symmetric Biphenyls. 1,4-Bis(carbazolyl)biphenyl (CCB). CCB was synthesized from 4,4′-diiodobiphenyl and carbazole using method 2, yielding 8.25 g (85%): ^{1}H NMR ($CDCl_3$) δ 8.16 (d, 4H, J = 7.7 Hz), 7.91 (d, 4H, J = 8.2 Hz), 7.70 (d, 4H, J = 8.2 Hz), 7.57−7.26 (m, 12H); MS m/z 484 (M^+, 100), 315 (7), 242 (M^{2+}, 54), 152 (7); Abs λ_{max} = 255, 295, 320 nm; E_{mm} λ_{max} = 389 nm.

1,4-Bis(1-naphthylphenylamino)biphenyl ($N_\alpha N_\alpha B$). $N_\alpha N_\alpha B$ was synthesized from 4,4′-dibromobiphenyl and 1-naphthylphenylamine using method 1, yielding 13.43 g (67%): ^{1}H NMR ($CDCl_3$) δ 7.75 (d, 2H, J = 7.9 Hz), 7.86 (d, 2H, J = 7.9 Hz), 7.75 (d, 2H, J = 7.9 Hz) 7.51−6.83 (m, 26H); MS m/z 588 (M^+, 100), 294 (M^{2+}, 26), 217 (10); Abs λ_{max} = 270, 340 nm; E_{mm} λ_{max} = 450 nm.

1,4-Bis(2-naphthylphenylamino)biphenyl ($N_\beta N_\beta B$). $N_\beta N_\beta B$ was synthesized from 4,4′-dibromobiphenyl and 2-naphthylphenylamine using method 1, yielding 2.35 g (10%): ^{1}H NMR ($CDCl_3$) δ 7.80 (t, 4H, J = 9.2 Hz), 7.65 (d, 2H, J = 7.9 Hz), 7.59−7.17 (m, 24H), 7.11 (t, 2H, J = 6.7 Hz); MS m/z 588 (M^+, 100), 369 (15), 294 (M^{2+}, 84), 217 (33), 242 (19), 191 (20), 115 (10); Abs λ_{max} = 260, 300, 340 nm; E_{mm} λ_{max} = 450 nm.

1,4-Bis(diphenylamino)biphenyl (DDB). DDB was synthesized from 4,4′-dibromobiphenyl and diphenylamine using method 1, yielding 4.14 g (45%): ^{1}H NMR ($CDCl_3$) δ 7.39−6.84 (m, 28H); MS m/z 488 (M^+, 100), 319 (6), 244 (M^{2+}, 40), 167 (14), 77 (7); Abs λ_{max} = 315 (sh), 355 nm; E_{mm} λ_{max} = 395 nm.

1,4-Bis(phenyl-*m*-tolylamino)biphenyl (TTB). TTB was synthesized from 4,4′-dibromobiphenyl and 3-methyldiphenylamine using method 1, yielding 3.72 g (30%): ^{1}H NMR ($CDCl_3$) δ 7.43 (d, 4H, J = 8.5 Hz), 7.30−6.80 (m, 22H), 2.30 (s, 6H); MS m/z 516 (M^+, 100), 333 (13), 258 (M^{2+}, 64), 167 (28), 77 (10); Abs λ_{max} = 315, 355 nm; E_{mm} λ_{max} = 396 nm.

1,4-Bis(iminodibenzyl)biphenyl (BBB). BBB was synthesized from 4,4′-dibromobiphenyl and iminodibenzyl using method 1, yielding 7.8 g (72%): ^{1}H NMR (acetone-d_6) δ 7.87 (d, 4H, J = 8.8 Hz), 7.64−6.17 (m, 8H), 3.03 (s, 4H), 2.99 (s, 4H); MS m/z 540 (M^+, 100), 270 (M^{2+}, 16), 194 (10); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 402 nm.

1,4-Bis(iminostilbenyl)biphenyl (SSB). SSB was synthesized from 4,4′-dibromobiphenyl and iminostilbene using method 1, yielding 206 g (38%): ^{1}H NMR ($CDCl_3$) δ 7.53−7.26 (m, 16H), 7.06 (d, 4H, J = 8.5 Hz), 6.80 (s, 4H), 6.25 (d, 4H, J = 8.5 Hz); MS m/z 536 (M^+, 100), 357 (11), 268 (M^{2+}, 72), 192 (52), 165 (30); Abs λ_{max} = 300, 340 (sh) nm; E_{mm} λ_{max} = 530 nm.

Singly Substituted Phenyl Halides. *N*-(4-Bromophenyl)-carbazole (BrCP). BrCP was synthesized from 1,4-dibromobenzene and carbazole using method 1, yielding about 65 g (70%): ^{1}H NMR (acetone-d_6) δ 8.24 (d, 2H), 7.85 (d, 2H), 7.60 (d, 2H), 7.48−7.24 (m, 6H); GCMS m/z 323 (M^+, 100), 321 (M^+, 100), 241 (50), 121 (25).

***N*-(4-Bromophenyl)-1-naphthylphenylamine ($BrN_\alpha P$).** $BrN_\alpha P$ was synthesized from 1,4-dibromobenzene and 1-naphthylphenylamine using method 1, yielding 1.9 g (59%): ^{1}H NMR ($CDCl_3$) δ 7.91 (d, 1H), 7.81 (d, 1H), 7.55−6.93 (m, ca. 12H), 6.88 (d, 2H); MS m/z 375 (M^+, 100), 373 (M^+, 100), 293 (34), 216 (56), 127 (17), 77 (30).

***N*-(4-Bromophenyl)-2-naphthylphenylamine ($BrN_\beta P$).** $BrN_\beta P$ was synthesized from 1,4-dibromobenzene and 2-naphthylphenylamine using method 1, yielding 1.9 g (59%): ^{1}H NMR ($CDCl_3$) δ 7.73 (t, 2H), 7.58 (d, 1H), 7.47−6.93 (m, ca. 13H); MS m/z 375 (M^+, 97), 373 (M^+, 97), 293 (40), 216 (100), 184 (46), 127 (36), 77 (93).

***N*-(4-Iodophenyl)diphenylamine (IDP).** IDP was synthesized from 1,4-diiodobenzene and diphenylamine using method 2, yielding 2.9 g (35%): ^{1}H NMR ($CDCl_3$) δ 7.34−6.87 (m, ca. 14H); MS m/z 371 (M^+, 100), 243 (39), 167 (58), 166 (70), 77 (78).

***N*-(4-Bromophenyl)phenyl-*m*-tolylamine(BrTP).** BrTP was synthesized from *p*-bromoiodobenzene and 3-methyldiphenylamine using method 2, yielding 2.6 g (30%): ^{1}H NMR ($CDCl_3$) δ 7.34−6.79 (m, ca. 13H), 2.24 (s, 3H); MS m/z 385

(M^+, 59), 339 (100), 337 (100), 257 (75), 180 (66), 152 (31), 128 (47), 77 (60).

***N*-(4-Bromophenyl)iminostilbene(BrSP).** BrSP was synthesized from 1,4-dibromobenzene and iminostilbene using method 1, yielding 2.2 g (40%): ^{1}H NMR ($CDCl_3$) δ 7.58−7.28 (m, ca. 9H), 7.03 (d, 2H), 6.80 (s, 1H), 6.11 (d, 2H); MS *m*/*z* 349 (M^+, 100), 347 (M^+, 100), 267 (63), 192 (77), 178 (77), 134 (68).

Singly Substituted Biphenyl Halides. 4-Iodo-4-(carbazolyl)biphenyl (ICB). ICB was synthesized from 4,4′-diiodobiphenyl and carbazole using method 2, yielding about 6.4 g (64%): ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 2H), 7.82 (d, 2H), 7.77 (d, 2H), 7.63 (d, 2H), 7.50−7.24 (m, 8H); MS *m*/*z* 445 (M^+, 68), 318 (70), 241 (12), 166 (50), 152 (100).

4-Iodo-4′-(1-naphthylphenylamino)biphenyl ($IN_\alpha B$). $IN_\alpha B$ was synthesized from 4,4′-diiodobiphenyl and 1-naphthylphenylamine using method 2, yielding about 4.9 g (42%): ^{1}H NMR ($CDCl_3$) δ 7.92 (d, 1H), 7.88 (d, 1H), 7.78 (d, 1H), 7.68 (d, 2H), 7.53−6.90 (m, ca. 15H); MS *m*/*z* 497 (M^+, 31), 370 (9), 293 (17), 241 (18), 217 (40), 152 (30), 127 (32), 77 (100).

4-Iodo-4′-(2-naphthylphenylamino)biphenyl ($IN_\beta B$). $IN_\beta B$ was synthesized from 4,4′-diiodobiphenyl and 2-naphthylphenylamine using method 2, yielding about 5.9 g (50%): ^{1}H NMR ($CDCl_3$) δ 7.73 (t, 4H), 7.58 (d, 2H), 7.47−6.94 (m, ca. 14H); MS *m*/*z* 497 (M^+, 100), 370 (68), 293 (62), 241 (48), 217 (83), 152 (57), 127 (40), 77 (72).

4-Iodo-4′-diphenylaminobiphenyl (IDB). IDB was synthesized from 4,4′-diiodobiphenyl and diphenylamine using method 2, yielding about 5.7 g (54%): ^{1}H NMR ($CDCl_3$) δ 7.44−7.19 (m, ca. 14H); MS *m*/*z* 447 (M^+, 100), 320 (16), 241 (19), 167 (15), 77 (21).

4-Iodo-4′-(phenyl-*m*-tolylamino)biphenyl (ITB). ITB was synthesized from 4,4′-diiodobiphenyl and 3-methyldiphenylamine using method 2, yielding ∼2.0 g (46%): ^{1}H NMR ($CDCl_3$) δ 7.73 (d, 2H), 7.41 (d, 2H), 7.34−6.83 (m, ca. 13H), 2.27 (s, 3H); MS *m*/*z* 461 (M^+, 2), 335 (100), 293 (10), 243 (10), 167 (12), 150 (20).

4-Iodo-4′-(iminodibenzyl)biphenyl (IBB). IBB was synthesized from 4,4′-diiodobiphenyl and iminodibenzyl using method 2, yielding ∼2.2 g (40%): ^{1}H NMR ($CDCl_3$) δ 7.66 (d, 2H), 7.46−7.16 (m, ca. 12H), 6.63 (dd, 2H), 3.00 (s, 4H); MS *m*/*z* 473 (M^+, 22), 346 (16), 152 (100), 77 (42).

4-Bromo-4′-(iminostilbenyl)biphenyl (BrSB). ISB was synthesized from 4,4′-dibromobiphenyl and iminostilbene using method 1, yielding ∼3.0 g (45%): ^{1}H NMR ($CDCl_3$) δ 7.52−7.15 (m, ca. 14H), 6.83 (s, 2H), 6.32 (d, 2H); MS *m*/*z* 425 (M^+, 100), 423 (M^+, 100), 345 (34), 191 (47), 177 (28), 152 (40).

Asymmetric Phenyls. 1-Carbazolyl-4-(1-naphthylphenylamino)benzene (N_αCP). N_αCP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and 1-naphthylphenylamine using method 1, yielding 0.72 g (50%): ^{1}H NMR (acetone-d_6) δ 8.18 (d, 2H), 8.10−7.99 (m, 2H), 7.94 (d, 2H), 7.67−7.12 (m, ca. 18H), 7.02 (t, 1H); MS *m*/*z* 460 (M^+, 100), 293 (30), 242 (13), 230 (M^{2+}, 57), 216 (26), 191 (12), 166 (21), 77 (6); Abs λ_{max} = 320, 350 nm; E_{mm} λ_{max} = 416 nm.

1-Carbazolyl-4-(2-naphthylphenylamino)benzene (N_βCP). N_βCP was synthesized from *N*-(4-bromophenyl)-carbazole (BrCP) and 2-naphthylphenylamino using method 1, yielding 1.02 g (71%): ^{1}H NMR (acetone-d_6) δ 8.20 (d, 2H), 7.87 (t, 2H), 7.73 (d, 2H), 7.63−7.18 (m, ca. 17H), 7.10 (t, 1H); MS *m*/*z* 460 (M^+, 100), 293 (8), 242 (3), 230 (M^{2+}, 15), 216 (5), 166 (3), 77 (2); Abs λ_{max} = 285, 295, 320 nm; E_{mm} λ_{max} = 409 nm.

1-Carbazolyl-4-(diphenylamino)benzene (DCP). DCP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and diphenylamine using method 1, yielding 0.54 g (42%): ^{1}H NMR (acetone-d_6) δ 8.20 (d, 2H), 7.53−7.05 (m, ca. 20H); MS *m*/*z* 410 (M^+, 100), 243 (9), 241 (8), 205 (M^{2+}, 17), 166 (9), 77 (3); Abs λ_{max} = 295, 320 nm; E_{mm} λ_{max} = 400 nm.

1-Carbazolyl-4-(phenyl-*m*-tolylamino)benzene (TCP). TCP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and 3-methyldiphenylamine using method 1, yielding 0.83 g (63%): ^{1}H NMR (acetone-d_6) δ 8.13 (d, 2H), 7.47−7.15 (m, ca. 15H), 6.89 (d, 1H), 2.30 (s, 3H); MS *m*/*z* 424 (M^+, 100), 258 (6), 241 (6), 212 (M^{2+}, 13), 181 (3), 166 (6); Abs λ_{max} = 295, 315 nm; E_{mm} λ_{max} = 370 nm.

1-Carbazolyl-4-(iminodibenzyl)benzene (BCP). BCP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and iminodibenzyl using method 1, yielding 0.96 g (71%): ^{1}H NMR (acetone-d_6) δ 8.17 (d, 2H), 7.52 (d, 2H), 7.48−7.16 (m, ca. 14H), 6.76 (d, 2H), 3.08 (s, 4H); MS *m*/*z* 436 (M^+, 100), 268 (5), 241 (7), 218 (13), 194 (10), 166 (3); Abs λ_{max} = 295 nm; E_{mm} λ_{max} = 382 nm.

1-Carbazole-4-(iminostilbenyl)benzene (SCP). SCP was synthesized from *N*-(4-bromophenyl)carbazole (BrCP) and iminostilbene using method 1, yielding 0.75 g (56%): ^{1}H NMR (acetone-d_6) δ 8.14 (d, 2H), 7.69−7.13 (m, ca. 16H), 6.99 (s, 2H), 6.44 (d, 2H); MS *m*/*z* 434 (M^+, 100), 268 (7), 255 (10), 242 (5), 217 (M^{2+}, 15), 192 (5), 165 (4); Abs λ_{max} = 270, 300 nm; E_{mm} λ_{max} = 393, 487 nm. Anal. Calcd for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10; N, 6.45. Found: C, 87.53; H, 5.74; N, 6.32.

1-(1-Naphthylphenylamino)-4-(2-naphthylphenylamino)benzene ($N_\beta N_\alpha$P). $N_\beta N_\alpha$P was synthesized from *N*-(4-bromophenyl)-1-naphthylphenylamine (BrN_αP) and 2-naphthylphenylamine using method 1, yielding 0.43 g (63%): ^{1}H NMR ($CDCl_3$) δ 7.96 (d, 1H), 7.87 (d, 1H), 7.81−6.83 (m, ca. 26H); MS *m*/*z* 512 (M^+, 100), 385 (2), 293 (23), 256 (M^{2+}, 51), 217 (59), 191 (12), 127 (11), 77 (13); Abs λ_{max} = 280, 320 nm; E_{mm} λ_{max} = 399, 496 nm.

1-(1-Naphthylphenylamino)-4-(diphenylamino)benzene (DN_αP). DN_αP was synthesized from *N*-(4-bromophenyl)-1-naphthylphenylamine (BrN_αP) and diphenylamine using method 1, yielding 0.48 g (77%): ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 1H), 7.87 (d, 1H), 7.74 (d, 1H), 7.52−6.79 (m, ca. 23H); MS *m*/*z* 462 (M^+, 100), 293 (10), 242 (11), 217 (38), 167 (40), 127 (20), 77 (78); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 414, 501 nm.

1-(1-Naphthylphenylamino)-4-(phenyl-*m*-tolylamino)benzene (TN_αP). TN_αP was synthesized *N*-(4-bromophenyl)-1-naphthylphenylamine (BrN_αP) and 3-methyldiphenylamine using method 1, yielding 0.37 g (58%): ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 1H), 7.87 (d, 1H), 7.75 (d, 1H), 7.52−6.82 (m, ca. 21H), 6.77 (d, 1H), 2.24 (s, 3H); MS *m*/*z* 476 (M^+, 100), 293 (21), 257 (14), 238 (M^{2+}, 60), 217 (50), 167 (43), 127 (11), 77 (22); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 417, 506 nm.

1-(1-Naphthylphenylamino)-4-(iminodibenzyl)benzene (BN_αP). BN_αP was synthesized *N*-(4-bromophenyl)-1-naphthylphenylamine (BrN_αP) and iminodibenzyl using method 1, yielding 0.31 g (67%): ^{1}H NMR ($CDCl_3$) δ 7.93 (d, 1H), 7.81 (d, 1H), 7.67 (d, 1H), 7.47−7.10 (m, ca. 15H), 6.90 (d, 2H), 6.76 (d, 2H), 6.45 (d, 2H), 2.98 (s, 4H); MS *m*/*z* 488 (M^+, 100), 308 (4), 294 (16), 268 (16), 244 (M^{2+}, 55), 217 (21), 194 (23), 127 (6), 77 (8); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 398, 510 nm.

1-(1-Naphthylphenylamino)-4-(iminostilbenyl)benzene (SN_αP). SN_αP was synthesized from *N*-(4-bromophenyl)-iminostilbene (BrSP) and 1-naphthylphenylamine using method 1, yielding 0.44 g (63%): ^{1}H NMR ($CDCl_3$) δ 7.98 (d, 1H), 7.90 (d, 1H), 7.66 (d, 1H), 7.59−6.65 (m, ca. 19H), 6.39 (d, 2H), 6.19 (d, 2H); MS *m*/*z* 486 (M^+, 100), 293 (3), 267 (3), 243 (M^{2+}, 27), 192 (17), 127 (3), 77 (7); Abs λ_{max} = 300, 350 nm; E_{mm} λ_{max} = 407 nm.

1-(2-Naphthylphenylamino)-4-(diphenylamino)benzene (DN_βP). DN_βP was synthesized from *N*-(4-bromophenyl)-2-naphthylphenylamine (BrPP) and diphenylamine using method 1, yielding 0.33 g (53%): ^{1}H NMR ($CDCl_3$) δ 7.71 (t, 2H), 7.89 (d, 1H), 7.44−6.93 (m, ca. 23H); MS *m*/*z* 462 (M^+, 100), 385 (3), 293 (30), 243 (14), 231 (M^{2+}, 56), 217 (15), 167 (50), 127 (15), 77 (38); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 399, 475 (sh) nm.

1-(2-Naphthylphenylamino)-4-(phenyl-*m*-tolylamino)benzene (TN_βP). TN_βP was synthesized from *N*-(4-bromophenyl)-2-naphthylphenylamine (BrN_βP) and 2-methyldiphenylamine using method 1, yielding 0.46 g (73%): ^{1}H NMR ($CDCl_3$) δ 7.72 (t, 2H), 7.59 (d, 1H), 7.44−6.87 (m, ca. 21H), 6.82 (d, 1H), 2.27 (s, 3H); MS *m*/*z* 476 (M^+, 100), 293 (28), 238 (M^{2+}, 58), 217 (56), 167 (55), 127 (13), 77 (23); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 398, 470 nm.

1-(2-Naphthylphenylamino)-4-(iminodibenzyl)benzene (BN_βP). BN_βP was synthesized from *N*-(4-bromophenyl)-2-naphthylphenylamine (BrN_βP) and iminodibenzyl using

method 1, yielding 0.27 g (60%): ^{1}H NMR ($CDCl_3$) δ 7.76−6.85 (m, ca. 23H), 6.53 (d, 1H), 3.03 (s, 4H); MS *m*/*z* 488 (M^+, 100), 294 (10), 268 (10), 244 (M^{2+}, 36), 217 (20), 194 (23), 180 (13), 127 (8), 77 (9); Abs λ_{max} = 280, 320 nm; E_{mm} λ_{max} = 398, 475 nm.

1-(2-Naphthylphenylamino)-4-(iminostilbenyl)benzene (SN$_\beta$P). SN$_\beta$P was synthesized from *N*-(4-bromophenyl)-iminostilbene (BrN$_\beta$P) and 2-naphthylphenylamine using method 1, yielding 0.35 g (50%): ^{1}H NMR ($CDCl_3$) δ 7.76 (d, 1H), 7.60 (d, 1H), 7.55−6.82 (m, ca. 20H), 6.79 (d, 2H), 6.22 (d, 2H); MS *m*/*z* 486 (M^+, 100), 307 (5), 294 (4), 267 (4), 243 (M^{2+}, 14), 192 (14), 178 (4), 127 (4), 77 (4); Abs λ_{max} = 280, 315 nm; E_{mm} λ_{max} = 402 nm.

1-(Diphenylamino)-4-(phenyl-*m*-tolylamino)benzene (TDP). TDP was synthesized from *N*-(4-bromophenyl)phenyl-*m*-tolylamine (BrTP) and diphenylamine using method 1, yielding 0.35 g (59%): ^{1}H NMR ($CDCl_3$) δ 7.31−6.69 (m, ca. 23H), 2.25 (s, 3H); MS *m*/*z* 426 (M^+, 100), 257 (5), 243 (4), 213 (M^{2+}, 19), 166 (40), 77 (18); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 397 nm.

1-(Diphenylamino)-4-(iminodibenzyl)benzene (BDP). BDP was synthesized from *N*-(4-iodophenyl)diphenylamine (IDP) and iminodibenzyl using method 1, yielding 0.30 g (50%): ^{1}H NMR ($CDCl_3$) δ 7.34−6.65 (m, ca. 20H), 6.65 (d, 2H), 3.03 (s, 4H); MS *m*/*z* 438 (M^+, 100), 360 (45), 219 (M^{2+}, 30).

1-(Diphenylamino)-4-(iminostilbenyl)benzene (SDP). SDP was synthesized from *N*-(4-bromophenyl)iminostilbene (BrDP) and diphenylamine using method 1, yielding 0.29 g (47%): ^{1}H NMR ($CDCl_3$) δ 7.51−6.70 (m, ca. 20H), 6.75 (d, 2H), 6.20 (d, 2H); MS *m*/*z* 436 (M^+, 100), 359 (5), 268 (13), 257 (21), 218 (M^{2+}, 27), 192 (22), 178 (12), 77 (13); Abs λ_{max} = 310 nm; E_{mm} λ_{max} = 398 nm.

1-(Phenyl-*m*-tolylamino)-4-(iminodibenzyl)benzene (BTP). BTP was synthesized from *N*-(4-bromophenyl)phenyl-*m*-tolylamine (BrTP) and iminodibenzyl using method 1, yielding 0.36 g (58%): ^{1}H NMR ($CDCl_3$) δ 7.41 (d, 2H), 7.32−6.65 (m, ca. 17H), 6.49 (d, 2H), 3.01 (s, 4H), 2.21 (s, 3H); MS *m*/*z* 452 (M^+, 38), 178 (100), 152 (37), 77 (92); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 398 nm.

1-(Phenyl-*m*-tolylamino)-4-(iminostilbenyl)benzene (STP). STP was synthesized from *N*-(4-bromophenyl)iminostilbene (BrTP) and 3-methyldiphenylamine using method 1, yielding 0.37 g (57%): ^{1}H NMR ($CDCl_3$) δ 7.55−6.80 (m, ca. 19H), 6.77 (d, 2H), 6.19 (d, 2H), 2.19 (s, 3H); MS *m*/*z* 450 (M^+, 100), 271 (9), 257 (9), 225 (M^{2+}, 9), 192 (26), 178 (20), 165 (21), 77 (16); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 400 nm.

1-(Iminodibenzyl)-4-(iminostilbenyl)benzene (SBP). SBP was synthesized from *N*-(4-bromophenyl)iminostilbene (BrSP) and iminodibenzyl using method 1, yielding 0.38 g (57%): ^{1}H NMR ($CDCl_3$) δ 7.48−7.04 (m, ca. 16H), 6.78 (s, 2H), 6.33 (d, 2H), 6.08 (d, 2H), 2.93 (s, 4H); MS *m*/*z* 462 (M^+, 100), 284 (15), 268 (33), 231 (M^{2+}, 60), 192 (52), 178 (39), 165 (32); Abs λ_{max} = 310 nm; E_{mm} λ_{max} = 395 nm. Anal. Calcd for $C_{34}H_{26}N_2$: C, 88.28; H, 5.67; N, 6.06. Found: C, 87.13; H, 5.57; N, 5.94.

Asymmetric Biphenyls. 4-Carbazolyl-4′-(1-naphthylphenylamino)biphenyl (N$_\alpha$CB). N$_\alpha$CB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and 1-naphthylphenylamine using method 1, yielding 0.37 g (54%): ^{1}H NMR ($CDCl_3$) δ 8.21−6.92 (m, ca. 28H); MS *m*/*z* 536 (M^+, 38), 342 (10), 240 (50), 216 (100), 165 (46), 126 (40), 76 (50); Abs λ_{max} = 295, 320 nm; E_{mm} λ_{max} = 422 nm.

4-Carbazolyl-4′-(2-naphthylphenylamino)biphenyl (N$_\beta$CB). N$_\beta$CB was synthesized from 4-bromo-4′-(carbazolyl)-biphenyl (BrCB) and 2-naphthylphenylamine using method 1, yielding 0.41 g (61%): ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 2H), 7.82−7.16 (m, ca. 24H), 7.08 (t, 2H); MS *m*/*z* 536 (M^+, 100), 342 (8), 217 (62), 127 (32), 76 (25); Abs λ_{max} = 295, 320, 345 nm; E_{mm} λ_{max} = 404 nm.

4-Carbazolyl-4′-(diphenylamino)biphenyl (DCB). DCB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and diphenylamine using method 1, yielding 0.13 g (27%): ^{1}H NMR ($CDCl_3$) δ 8.22 (d, 2H), 7.98 (d, 1H), 7.91−7.18 (m, ca. 21H), 7.12 (t, 2H); MS *m*/*z* 486 (M^+, 100), 408 (2), 319 (7), 243 (M^{2+}, 37), 166 (4), 77 (2); Abs λ_{max} = 295, 340 nm; E_{mm} λ_{max} = 390 nm.

4-Carbazolyl-4′-(phenyl-*m*-tolylamino)biphenyl (TCB). TCB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and 3-methyldiphenylamine using method 1, yielding 0.35 g (70%): ^{1}H NMR ($CDCl_3$) δ 8.15 (d, 2H), 7.78 (d, 2H), 7.59 (d, 2H), 7.55 (d, 2H), 7.50−6.91 (m, ca. 16H), 6.88 (d, 1H), 2.28 (s, 3H); MS *m*/*z* 500 (M^+, 100), 333 (10), 318 (7), 250 (M^{2+}, 62), 166 (12); Abs λ_{max} = 295, 345 nm; E_{mm} λ_{max} = 400 nm.

4-Carbazolyl-4′-(iminodibenzyl)biphenyl (BCB). BCB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and iminodibenzyl using method 1, yielding 0.27 g (56%): ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 2H), 7.76−7.20 (m, ca. 20H), 6.70 (d, 2H), 3.04 (s, 4H); MS *m*/*z* 512 (M^+, 100), 256 (M^{2+}, 19), 194 (11), 167 (5), 152 (6); Abs λ_{max} = 295, 325 nm; E_{mm} λ_{max} = 373 nm. Anal. Calcd for $C_{40}H_{32}N_2$: C, 89.03; H, 5.51; N, 5.46. Found: C, 88.28; H, 5.36; N, 5.33.

4-Carbazolyl-4′-(iminostilbenyl)biphenyl (SCB). SCB was synthesized from 4-bromo-4′-(carbazolyl)biphenyl (BrCB) and iminostilbene using method 1, yielding 0.42 g (73%): ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 2H), 7.72−7.22 (m, ca. 20H), 6.87 (s, 2H), 6.41 (d, 2H); MS *m*/*z* 510 (M^+, 100), 343 (11), 332 (10), 315 (13), 255 (M^{2+}, 70), 192 (40), 178 (15), 166 (57), 152 (28), 139 (12); Abs λ_{max} = 295, 315 nm; E_{mm} λ_{max} = 386 nm. Anal. Calcd for $C_{38}H_{26}N_2$: C, 89.38; H, 5.13; N, 5.49. Found: C, 89.27; H, 5.07; N, 5.49.

4-(1-Naphthylphenylamino)-4′-(2-naphthylphenylamino)biphenyl (N$_\beta$N$_\alpha$B). PN$_\alpha$B was synthesized from 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN$_\alpha$B) and 2-naphthylphenylamine using method 2, yielding 0.45 g (38%): ^{1}H NMR ($CDCl_3$) δ 7.94 (d, 1H), 7.87 (d, 1H), 7.81−6.86 (m, ca. 30H); MS *m*/*z* 588 (M^+, 100), 369 (3), 294 (M^{2+}, 40), 217 (27), 77 (5); Abs λ_{max} = 340 nm; E_{mm} λ_{max} = 431 nm.

4-(1-Naphthylphenylamino)-4′-(diphenylamino)biphenyl (DN$_\alpha$B). DN$_\alpha$B was synthesized from 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN$_\alpha$B) and diphenylamine using method 2, yielding 0.28 g (43%): ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 1H), 7.88 (d, 1H), 7.83−6.85 (m, ca. 28H); MS *m*/*z* 538 (M^+, 100), 369 (3), 269 (M^{2+}, 34), 217 (9), 167 (8), 77 (3); Abs λ_{max} = 310, 350 nm; E_{mm} λ_{max} = 400 (sh), 450 nm.

4-(1-Naphthylphenylamino)-4′-(phenyl-*m*-tolylamino)biphenyl (TN$_\alpha$B). TN$_\alpha$B was synthesized from 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN$_\alpha$B) and 3-methyldiphenylamine using method 2, yielding 0.24 g (36%): ^{1}H NMR ($CDCl_3$) δ 7.93 (d, 1H), 7.86 (d, 1H), 7.81−6.75 (m, ca. 27H), 2.15 (s, 3H); MS *m*/*z* 552 (M^+, 100), 332 (1), 276 (M^{2+}, 25), 217 (7), 167 (5), 77 (3); Abs λ_{max} = 315, 350 nm; E_{mm} λ_{max} = 450 nm.

4-(1-Naphthylphenylamino)-4′-(iminodibenzyl)biphenyl (BN$_\alpha$B). BN$_\alpha$B was synthesized from 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN$_\alpha$B) and iminodibenzyl using method 2, yielding 0.36 g (32%): ^{1}H NMR ($CDCl_3$) δ 7.96 (d, 1H), 7.89 (d, 1H), 7.82 (d, 1H), 7.75 (d, 1H), 7.55−6.82 (m, ca. 21H), 6.59 (d, 2H), 2.99 (s, 4H); MS *m*/*z* 564 (M^+, 100), 369 (5), 344 (3), 282 (M^{2+}, 37), 217 (16), 194 (21), 77 (5). Anal. Calcd for $C_{42}H_{32}N_2$: C, 89.33; H, 5.71; N, 4.96. Found: C, 88.55; H, 5.37; N, 4.55.

4-(1-Naphthylphenylamino)-4′-(iminostilbenyl)biphenyl (SN$_\alpha$B). SN$_\alpha$B was synthesized using 4-iodo-4′-(1-naphthylphenylamino)biphenyl (IN$_\alpha$B) and iminostilbene using method 1, yielding 0.23 g (79%): ^{1}H NMR ($CDCl_3$) δ 7.91 (d, 1H), 7.85 (d, 1H), 7.73 (d, 1H), 7.53−6.79 (m, ca. 25H), 6.29 (d, 2H); MS *m*/*z* 562 (M^+, 100), 281 (M^{2+}, 50), 217 (10), 192 (17), 165 (8); Abs λ_{max} = 270, 330 nm; E_{mm} λ_{max} = 404, 507 (br) nm. Anal. Calcd for $C_{42}H_{30}N_2$: C, 89.65; H, 5.37; N, 4.98. Found: C, 87.95; H, 5.32; N, 4.82.

4-(2-Naphthylphenylamino)-4′-(diphenylamino)biphenyl (DN$_\beta$B). DN$_\beta$B was synthesized from 4-iodo-4′-(diphenylamino)biphenyl (IDB) and 2-naphthylphenylamine using method 2, yielding 0.37 g (31%): ^{1}H NMR ($CDCl_3$) δ 7.81 (t, 2H), 7.67 (d, 1H), 7.58−7.03 (m, ca. 27H); MS *m*/*z* 538 (M^+, 100), 369 (8), 269 (M^{2+}, 58), 217 (23), 167 (12), 77 (9); Abs λ_{max} = 320, 350 nm; E_{mm} λ_{max} = 417 nm.

4-(2-Naphthylphenylamino)-4′-(phenyl-*m*-tolylamino)-biphenyl (TN$_\beta$B). TN$_\beta$B was synthesized from 4-iodo-4′-(2-naphthylphenylamino)biphenyl (IN$_\beta$B) and 3-methyldiphenylamine using method 2, yielding 0.49 g (44%): ^{1}H NMR ($CDCl_3$) δ 7.73 (t, 2H), 7.59 (d, 1H), 7.52−6.80 (m, ca. 26H), 2.26 (s, 3H); MS *m*/*z* 552 (M^+, 100), 369 (10), 276 (M^{2+}, 95), 216 (76), 166 (47), 77 (40); Abs λ_{max} = 320, 350 nm; E_{mm} λ_{max} = 415 nm.

4-(2-Naphthylphenylamino)-4′-(iminodibenzyl)biphenyl (BN$_\beta$B). BN$_\beta$B was synthesized from 4-iodo-4′-(iminodibenzyl)biphenyl (IBB) and 2-naphthylphenylamine using method 2, yielding 0.27 g (25%): ^{1}H NMR ($CDCl_3$) δ 7.76−6.94 (m, ca. 26H), 6.62 (d, 2H), 3.00 (s, 4H); MS *m*/*z* 564 (M^+, 100), 368 (15), 296 (15), 282 (M^{2+}, 14), 217 (5), 77 (3); Abs λ_{max} = 330 nm; E_{mm} λ_{max} = 414 nm.

4-(2-Naphthylphenylamino)-4′-(iminostilbenyl)biphenyl (SN$_\beta$B). SN$_\beta$B was synthesized from 4-iodo-4′-(2-naphthylphenylamino)biphenyl (IN$_\beta$B) and iminostilbene using method 1, yielding 0.37 g (73%): ^{1}H NMR ($CDCl_3$) δ 7.81−6.95 (m, ca. 26H), 6.83 (s, 2H), 6.33 (d, 2H); MS *m*/*z* 562 (M^+, 100), 369 (3), 281 (M^{2+}, 32), 217 (13), 192 (18), 77 (3); Abs λ_{max} = 280, 330 nm; E_{mm} λ_{max} = 413, 518 (w,br) nm. Anal. Calcd for $C_{42}H_{30}N_2$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.54; H, 5.43; N, 4.87.

4-(Diphenylamino)-4′-(phenyl-*m*-tolylamino)biphenyl (TDB). TDB was synthesized from 4-iodo-4′-(diphenylamino)biphenyl (IDB) and 3-methyldiphenylamine using method 1, yielding 0.45 g (80%): ^{1}H NMR ($CDCl_3$) δ 7.48−6.80 (m, ca. 27H), 2.25 (s, 3H); MS *m*/*z* 502 (M^+, 100), 333 (8), 319 (7), 251 (M^{2+}, 68), 167 (15), 77 (8); Abs λ_{max} = 310, 350 nm; E_{mm} λ_{max} = 396 nm.

4-(Diphenylamino)-4′-(iminodibenzyl)biphenyl (BDB). BDB was synthesized from 4-iodo-4′-(diphenylamino)biphenyl (IDB) and iminodibenzyl using method 1, yielding 0.26 g (51%): ^{1}H NMR ($CDCl_3$) δ 7.46−6.93 (m, ca. 24H), 6.62 (d, 2H), 3.00 (s, 4H); MS *m*/*z* 514 (M^+, 100), 257 (M^{2+}, 24), 194 (10), 167 (8), 77 (3); Abs λ_{max} = 340 nm; E_{mm} λ_{max} = 400 nm.

4-(Diphenylamino)-4′-(iminostilbenyl)biphenyl (SDB). SDB was synthesized from 4-bromo-4′-(iminostilbenyl)biphenyl (BrSB) and diphenylamine using method 1, yielding 0.64 g (53%): ^{1}H NMR ($CDCl_3$) δ 7.58−6.90 (m, ca. 24H), 6.83 (s, 2H), 6.31 (d, 2H); MS *m*/*z* 512 (M^+, 100), 256 (M^{2+}, 17), 192 (20), 192 (20), 178 (18), 165 (16), 152 (8), 77 (10); Abs λ_{max} = 310 (sh), 330 nm; E_{mm} λ_{max} = 397, 513 (br) nm.

4-(Phenyl-*m*-tolylamino)-4′-(iminodibenzyl)biphenyl (BTB). BTB was synthesized from 4-iodo-4′-(iminodibenzyl)-biphenyl (IBB) and 3-methyldiphenylamine using method 2, yielding 0.28 g (25%): ^{1}H NMR ($CDCl_3$) δ 7.45−6.85 (m, ca. 22H), 6.80 (d, 1H), 2.99 (s, 4H), 2.23 (s, 3H); MS *m*/*z* 528 (M^+, 67), 348 (17), 194 (66), 179 (74), 178 (100), 151 (38), 77 (32); Abs λ_{max} = 340 nm; E_{mm} λ_{max} = 402 nm.

4-(Phenyl-*m*-tolylamino)-4′-(iminostilbenyl)biphenyl (STB). STB was synthesized from 4-iodo-4′-(iminostilbene)-biphenyl (ISB) and 3-methyldiphenylamine using method 1, yielding 0.55 g (44%): ^{1}H NMR ($CDCl_3$) δ 7.53−6.76 (m, ca. 25H), 6.31 (d, 2H), 2.23 (s, 3H); MS *m*/*z* 526 (M^+, 100), 263 (M^{2+}, 9), 193 (28), 178 (29), 152 (10), 77 (8); Abs λ_{max} = 310 (sh), 340 nm; E_{mm} λ_{max} = 397, 517 nm.

4-(Iminodibenzyl)-4′-(iminostilbenyl)biphenyl (SBB). SBB was synthesized from 4-iodo-4′-(iminostilbenyl)biphenyl (ISB) and iminodibenzyl using method 1, yielding 0.30 g (48%): ^{1}H NMR ($CDCl_3$) δ 7.08−7.56 (m, ca. 20H), 6.82 (s, 2H), 6.57 (d, 2H), 6.29 (d, 2H), 2.98 (s, 4H); MS *m*/*z* 538 (M^+, 100), 344 (6), 269 (M^{2+}, 32), 194 (16), 192 (20), 178 (13), 165 (12); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 411, 533 (w,br) nm. Anal. Calcd for $C_{40}H_{30}N_2$: C, 89.19; H, 5.61; N, 5.20. Found: C, 88.14; H, 5.62; N, 5.10.

Symmetric Phenyls. 1,4-Bis(carbazolyl)benzene (CCP). CCP was synthesized from 1,4-dibromobenzene and carbazole using method 1, yielding g (%): ^{1}H NMR ($CDCl_3$) δ 8.18 (d, 4H), 7.81 (s, 4H), 7.57 (d, 4H), 7.47 (t, 4H), 7.33 (t, 4H); MS *m*/*z* 408 (M^+, 100), 241 (4), 204 (M^{2+}, 50), 166 (8), 140 (8); Abs λ_{max} = 295, 310 nm; E_{mm} λ_{max} = 343 nm.

1,4-Bis(1-naphthylphenylamino)benzene (N$_\alpha$N$_\alpha$P). N$_\alpha$N$_\alpha$P was synthesized from 1,4-diiodobenzene and 1-naphthylphenylamine using method 2, yielding 15.3 g (26%): ^{1}H NMR ($CDCl_3$); MS *m*/*z* 512 (M^+, 100), 293 (10), 256 (M^{2+}, 32), 217 (30); Abs λ_{max} = 280, 320 nm; E_{mm} λ_{max} = 505 nm.

1,4-Bis(2-naphthylphenylamino)benzene (N$_\beta$N$_\beta$P). N$_\beta$N$_\beta$P was synthesized from 1,4-diiodobenzene and 2-naphthylphenylamine using method 2, yielding 2.15 g (52%): ^{1}H NMR ($CDCl_3$) δ; MS *m*/*z* 512 (M^+, 100), 369 (5), 293 (15), 256 (M^{2+}, 13), 217 (39), 191 (8), 127 (7), 77 (7); Abs λ_{max} = 260, 280, 325 nm; E_{mm} λ_{max} = 471 nm.

1,4-Bis(diphenylamino)benzene (DDP). DDP was synthesized from 1,4-dibromobenzene and diphenylamine using method 1, yielding g (%): ^{1}H NMR ($CDCl_3$) δ; MS *m*/*z* 412 (M^+, 100), 243 (9), 206 (M^{2+}, 9), 167 (44), 77 (30); Abs λ_{max} = nm; E_{mm} λ_{max} = nm.

1,4-Bis(phenyl-*m*-tolylamino)benzene (TTP). TTP was synthesized from 3-iodotoluene and N,N′-diphenyl-1,4-phenylenediamine using method 2, yielding 2.66 g (76%): ^{1}H NMR ($CDCl_3$) δ; MS *m*/*z* 440 (M^+, 100), 256 (10), 220 (M^{2+}, 26), 166 (32), 77 (8); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 376 nm.

1,4-Bis(iminodibenzyl)benzene (BBP). BBP was synthesized from 1,4-dibromobenzene and iminodibenzyl using method 1, yielding 0.55 g (11%): ^{1}H NMR ($CDCl_3$) δ; MS *m*/*z* 464 (M^+, 100), 232 (M^{2+}, 17), 194 (16), 165 (10); Abs λ_{max} = 315 nm; E_{mm} λ_{max} = 368 nm.

1,4-Bis(iminostilbenyl)benzene (SSP). SSP was synthesized from 1,4-dibromobenzene and iminostilbene using method 1, yielding 1.3 g (47%): ^{1}H NMR ($CDCl_3$) δ; MS *m*/*z* 460 (M^+, 100), 280 (10), 230 (M^{2+}, 13), 192 (11), 165 (8); Abs λ_{max} = 290, 340 nm; E_{mm} λ_{max} = 444, 488 nm.

Symmetric Biphenyls. 1,4-Bis(carbazolyl)biphenyl (CCB). CCB was synthesized from 4,4′-diiodobiphenyl and carbazole using method 2, yielding 8.25 g (85%): ^{1}H NMR ($CDCl_3$) δ 8.16 (d, 4H), 7.91 (d, 4H), 7.70 (d, 4H), 7.57−7.26 (m, 12H); MS *m*/*z* 484 (M^+, 100), 315 (7), 242 (M^{2+}, 54), 152 (7); Abs λ_{max} = 255, 295, 320 nm; E_{mm} λ_{max} = 389 nm.

1,4-Bis(1-naphthylphenylamino)biphenyl (N$_\alpha$N$_\alpha$B). N$_\alpha$N$_\alpha$B was synthesized from 4,4′-dibromobiphenyl and 1-naphthylphenylamine using method 1, yielding 13.43 g (67%): ^{1}H NMR ($CDCl_3$) δ 7.75 (d 2H), 7.51−6.83 (m 30H); MS *m*/*z* 588 (M^+, 100), 294 (M^{2+}, 26), 217 (10); Abs λ_{max} = 270, 340 nm; E_{mm} λ_{max} = 450 nm.

1,4-Bis(2-naphthylphenylamino)biphenyl (N$_\beta$N$_\beta$B). N$_\beta$N$_\beta$B was synthesized from 4,4′-dibromobiphenyl and 2-naphthylphenylamine using method 1, yielding g (%): ^{1}H NMR ($CDCl_3$) δ 7.80 (t, 4H), 7.65 (d, 2H), 7.59−7.17 (m, 24H), 7.11 (t, 2H); MS *m*/*z* 588 (M^+, 100), 369 (15), 294 (M^{2+}, 84), 217 (33), 242 (19), 191 (20), 115 (10); Abs λ_{max} = 260, 300, 340 nm; E_{mm} λ_{max} = 450 nm.

1,4-Bis(diphenylamino)biphenyl (DDB). DDB was synthesized from 4,4′-dibromobiphenyl and diphenylamine using method 1, yielding 4.14 g (45%): ^{1}H NMR ($CDCl_3$) δ; MS *m*/*z* 488 (M^+, 100), 319 (6), 244 (M^{2+}, 40), 167 (14), 77 (7); Abs λ_{max} = 315 (sh), 355 nm; E_{mm} λ_{max} = 395 nm.

1,4-Bis(phenyl-*m*-tolylamino)biphenyl (TTB). TTB was synthesized from 4,4′-dibromobiphenyl and 3-methyldiphenylamine using method 1, yielding 3.72 g (30%): ^{1}H NMR ($CDCl_3$) δ 7.43 (d, 4H), 7.30−6.80 (m, 22H), 2.30 (s, 6H); MS *m*/*z* 516 (M^+, 100), 333 (13), 258 (M^{2+}, 64), 167 (28), 77 (10); Abs λ_{max} = 315, 355 nm; E_{mm} λ_{max} = 396 nm.

1,4-Bis(iminodibenzyl)biphenyl (BBB). BBB was synthesized from 4,4′-dibromobiphenyl and iminodibenzyl using method 1, yielding 7.8 g (72%): ^{1}H NMR ($CDCl_3$) δ; MS *m*/*z* 540 (M^+, 100), 270 (M^{2+}, 16), 194 (10); Abs λ_{max} = 320 nm; E_{mm} λ_{max} = 402 nm.

1,4-Bis(iminostilbenyl)biphenyl (SSB). SSB was synthesized from 4,4′-dibromobiphenyl and iminostilbene using method 1, yielding 206 g (38%): ^{1}H NMR ($CDCl_3$) δ 7.53−7.26 (m, 16H), 7.06 (d, 4H), 6.80 (s, 4H), 6.25 (d, 4H); MS *m*/*z* 536 (M^+, 100), 357 (11), 268 (M^{2+}, 72), 192 (52), 165 (30); Abs λ_{max} = 300, 340 (sh) nm; E_{mm} λ_{max} = 530 nm.

Results and Discussion

Tetraarylphenylenediamines (e.g., Scheme 1, n = 1) and tetraarylbenzidines (e.g., Scheme 1, n = 2) have

been extensively investigated as hole transporting materials in xerographic and electroluminescent applications. These materials have the same amine groups bound to either end of the phenylene or biphenylene core. Two materials of this type that are commonly used in electroluminescent applications are TPD and NPD. These are typically prepared by an Ullmann condensation, which involves a copper-catalyzed coupling of an aryl halide and a diarylamine, eq 1. This

$$2Ar_1Ar_2NH + XAr'X \xrightarrow{Cu^0} Ar_1Ar_2NAr'NAr_1Ar_2 + 2HX \quad (1)$$

coupling reaction is problematic, producing irreproducible yields and product purities. An alternate synthesis of triarylamines has been developed that utilizes a Pd catalyst[25] and reacts under much milder conditions (100 °C for 8−24 h for the Pd-catalyzed reaction vs 190 °C for 2 days for the Ullmann route) to give a significantly purer product. Using both methods, we have prepared a number of symmetric materials for comparison to the asymmetric materials described below. The symmetric compounds fall along the diagonals of Table 1 and Table 2. For a few of these materials (i.e., CCP, CCB), Ullmann coupling reactions reproducibly afford reasonable yields. For most of the materials, however, the Pd-catalyzed coupling reactions are significantly more efficient.

The asymmetric phenylene- and biphenylenediamines reported here have been prepared in two steps. First, a diarylamine is treated with an excess of a dihaloarene (i.e., 1,4-dihalobenzene or 4,4′-dihalobiphenyl), eq 2.

$$Ar_1Ar_2NH + \text{excess } XAr'X \xrightarrow{\text{catalyst}} Ar_1Ar_2NAr'X + HX \quad (2)$$

Both Cu- and Pd-catalyzed reactions have been examined for this initial coupling reaction. For Cu-coupling reactions, the dihaloarene used was the diiodo derivative, while for the Pd-catalyzed couplings, the dibromo derivative was used. Excess dihaloarene was used to prevent the coupling of a second equivalent of amine to the dihaloarene. The excess dihaloarene was removed from the product by solvent extraction or sublimation. The singly substituted arene ($Ar_1Ar_2NAr'X$) was then purified by sublimation. The purified sample of $Ar_1Ar_2NAr'X$ was then coupled to a second amine, yielding the asymmetric diamine, eq 3, which was subsequently purified by sublimation.

$$Ar_3Ar_4NH + Ar_1Ar_2NAr'X \xrightarrow{\text{catalyst}} Ar_1Ar_2NAr'NAr_3Ar_4 + HX \quad (3)$$

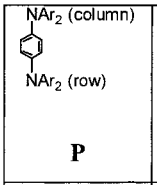
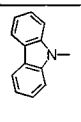
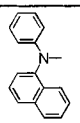
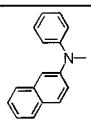
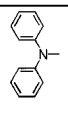
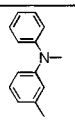
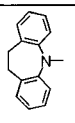
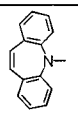
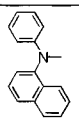
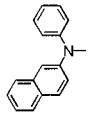
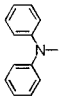
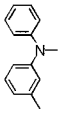
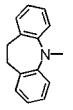
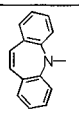
Thermal Properties. It is important for OLEDs to be constructed from materials that are stable glasses to avoid problems associated with grain boundaries in polycrystalline films and to achieve the highest level of uniformity in the vapor-deposited thin films. Many organic molecules can be induced into a glassy state. This occurs when the liquid form of the substance is cooled quickly enough to solidify the sample prior to crystallization.[27] The temperature (or temperature range) where the glass becomes less viscous as it is heated is referred to as the glass transition temperature (T_g). At a temperature above the T_g, the material may crystallize followed by a melting transition at an even higher temperature. It is possible that crystallization may not be observed at all in a given material for kinetic reasons, such that the glass smoothly transforms from a glass to a liquid. Some molecules have greater glass-forming ability than others do. In general, glasses that are stable at high temperatures are formed by asymmetric molecules with reasonably high molecular masses, which have no strong intermolecular forces such as hydrogen bonding. When the liquid sample is cooled rapidly, the molecules are frozen into an amorphous structure. The same amorphous structure is formed on vapor deposition of the materials since the substrate temperature is comparatively cold. Reorganization of this amorphous material to crystalline or polycrystalline material is hindered due to the high energy required to reorient the molecules into the proper crystalline arrangement. If the molecules are symmetric, the amount of molecular reorganization needed to achieve the crystalline structure is low and the material readily crystallizes. Similarly, if the molecules are small, the energy required to reorient the molecules is low and crystallization may occur at a low temperature. The last requirement, listed above for stable glasses (i.e., there are no strong intermolecular forces), is very important. If strong intermolecular forces exist, they may significantly increase the lattice energies helping to drive the material to a crystalline form. In addition, the intermolecular forces can lead to preassociation of the molecules into crystalline aggregates before the melt cools, or while the film is being deposited from vapor. These aggregates can then nucleate crystal growth, preventing the formation of a glass. One of our goals is to understand or draw some general correlations between molecular structure and glass transitions. Foremost though is to improve thermal stability for HTL candidates while retaining their favorable electronic properties.

Most of the asymmetric compounds prepared offer improved thermal stability over TPD; see Tables 1 abd 2. As a general trend, the biphenyl derivatives have a higher T_g than the single phenyl derivatives. Compounds such as CCB do not form glasses due to the high level of symmetry and their largely planar structures. Higher T_gs are obtained for materials containing the amines iminostilbene, iminodibenzyl, and/or carbazole. These amines have a hydrocarbon linkage or single bond joining the arene groups, preventing free rotation about the *N*-phenyl bond. Consequently, the ones having two of these three groups incorporated into the molecule have the highest T_gs (SCB, SBB, SSB, and BCB).

A typical DSC for these asymmetric diamines is shown in Figure 2. This plot shows the initial scan of SCB and subsequent heating cycles. Upon first heating no glass transition is observed. This is not surprising since the slow rate of cooling upon sublimation (used to purify the materials) tends to lead to crystalline materials. Once the sample is melted and cooled to room

(27) Murthy, S. S. N.; Gangasharan, Nayak, S. K. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 509.

Table 1. Thermal, redox, absorption, and Fluorescence Data as Well as the Acronym for Each of the Phenylenediamines Prepared[a]

 P	 C	 N_α	 N_β	 D	 T	 B	 S
	**CCP** 310/NA 1.041 295,310 343	**N_αCP** 215/88 0.945 320,350 416	**N_βCP** 212/83 0.947 285,295,320 409	**DCP** 158/61 0.965 295,320 400	**TCP** 139/54 0.950 295,315 370	**BCP** 233/91 0.958 295 382	**SCP** 259/103 1.008 270,300 393,487
		**$N_\alpha N_\alpha$P** 185/70 0.625 280, 320 505	**$N_\beta N_\alpha$ P** NA/81 0.616 280,320 399,496	**DN_αP** NA/62 0.611 320 414,501	**TN_αP** NA/60 0.595 320 417,506	**BN_αP** NA/85 0.551 315 398,510	**SN_αP** NA/96 0.591 300,350 407
			**$N_\beta N_\beta$P** 182/68 0.616 260,280,325 471	**DN_βP** NA/63 0.606 320 399,475	**TN_βP** NA/59 0.592 320 398,470	**BN_βP** NA/83 0.569 280,320 398,475	**SN_βP** NA/96 0.581 280,315 402
				**DDP** 290/NA 0.602 320,340 394	**TDP** 169/22 0.593 315 397	**BDP** 250/56 0.560 310,350 437	**SDP** NA/66 0.563 310 398
					**TTP** 175/39 0.561 315 376	**BTP** NA/54 0.534 320 398	**STP** NA/70 0.558 315 400
						**BBP** NA/73 0.416 315 368	**SBP** 265/109 0.492 310 395
							**SSP** 304 0.489 290,340 444,488

[a] The amine found in the column is bound to the 1 position of the benzene and the amine in the row is bound to the 4 position. The amines found along the diagonal are symmetric (i.e., the same amine is bound to both the 1 and 4 positions), while all of the nondiagonal entries are asymmetric (i.e., they have different amines bound to the 1 and 4 positions). The first line of each entry is the acronym for the given compound. The one-letter designations used for the amines are listed below each amine in the first row. The second line gives the melting point and glass transition (°C), listed mp/T_g. For the compounds in which a melting point or T_g were not observed the values are denoted NA. The third line is the oxidation potential (V) relative to Ag/AgCl. The fourth line gives the λ_{max} value(s) (nm) for the solution absorption spectra, and the last line gives the λ_{max} value(s) (nm) for the solution fluorescence spectra.

temperature, the second heating exhibits a glass transition at 125 °C. If heating is continued beyond the glass transition, a crystallization exotherm is observed. If the scan is stopped before the sample heated above the melt, the subsequent heating cycle will not show a T_g or a crystallization exotherm, as expected for a crystalline sample. However, once the sample is melted again and cooled, reemergence of the amorphous phase is seen. This behavior is typical for the asymmetric diamines. Several of the diamines, however, do not crystallize after going through their T_g. These molecules may offer improved lifetime in devices due to their excellent glass-forming ability (i.e., no crystallization over time). These compounds, including $SN_\alpha B$, STB, $BN_\alpha B$, and BBB, do not have a well-defined melt.

The asymmetric diamine compounds may also be used to induce glass formation of the symmetric derivatives. For example, CCB shows no glassy form in its DSC, but a sharp melt consistent with a polycrystalline material. Several of the asymmetric diamines have been doped into CCB at varying percentages and found to hinder crystallization. Using this method, a glass transition

Table 2. Thermal, Redox, Absorption, and Fluorescence Data as Well as the Acronym for Each of the Benzidines Prepared[a]

NAr$_2$ (column) / NAr$_2$ (row) **B**	**C**	**N$_\alpha$**	**N$_\beta$**	**D**	**T**	**B**	**S**
	CCB 290/NA 0.975 255,295,320 389	**N$_\alpha$CB** 253/109 1.003 295,330 422	**N$_\beta$CB** 249/107 0.994 295,320,345 404	**DCB** 217/91 0.975 295,340 390	**TCB** 198/85 0.925 295,345 400	**BCB** 273/117 0.992 295,325 373	**SCB** 291/125 1.040 295,315 386
		NPD (N$_\alpha$N$_\alpha$B) 265/100 0.767 270,340 450	**N$_\beta$N$_\alpha$B** NA/106 0.775 340 431	**DN$_\alpha$B** NA/87 0.779 310,350 400,440	**TN$_\alpha$B** NA/85 0.746 315,350 450	**BN$_\alpha$B** NA/110 0.709 345 434	**SN$_\alpha$B** NA/117 0.772 330 404,507(sh)
			N$_\beta$N$_\beta$B 265/103 0.794 260,300,340 450	**DN$_\beta$B** NA/92 0.780 320,350 417	**TN$_\beta$B** NA/94 0.750 320,350 415	**BN$_\beta$B** NA/105 0.737 330 414	**SN$_\beta$B** NA/117 0.733 280,330 413,518(sh)
				DDB 236/77 0.751 315,355 395	**TDB** 184/71 0.766 310,350 396	**BDB** NA/96 0.7334 340 400	**SDB** NA/97 0.746 330 397,513(sh)
					TPD (TTB) 175/60 0.733 315,355 396	**BTB** NA/86 0.702 340 402	**STB** NA/91 0.720 340 397,517(sh)
						BBB NA/117 0.664 320 402	**SBB** 295/125 0.691 320 411
							SSB 317/110 0.699 300,340(sh) 530

[a] The amine found in the column is bound to the 4 position of the biphenyl and the amine in the row is bound to the 4′ position. The amines found along the diagonal are symmetric (i.e., the same amine is bound to both the 4 and 4′ positions), while all of the nondiagonal entries are asymmetric (i.e., they have different amines bound to the 4 and 4′ positions). The first line of each entry is the acronym for the given compound. The one-letter designations used for the amines are listed below each amine in the first row. The second line gives the melting point and glass transition (°C), listed mp/T_g. For the compounds in which a melting point or T_g were not observed the values are denoted NA. The third line is the oxidation potential (V) relative to Ag/AgCl. The fourth line gives the λ_{max} value(s) (nm) for the solution absorption spectra, and the last line gives the λ_{max} value(s) (nm) for the solution fluorescence spectra.

for doped CBP of about 107 °C has been observed regardless of which diamine was used as the dopant. The DSC scans shown in Figure 3 illustrate the effect of doping of N$_\alpha$CP into CCB. The DSC scan shown at the bottom is for pure CBP and shows only a melt transition on the first and all subsequent scans. When CCB and 10% N$_\alpha$CP are ground together with a mortar and pestle, the DSC scan of the mixture shows two melting transitions on the first heating cycle at 195 and 264 °C, close to the melting temperatures of N$_\alpha$CP and CCB, respectively. When the sample is then cooled to room temperature and heated again, a distinct glass transition is observed at 107 °C, a crystallization at 145 °C, and a melt transition at 264 °C. The melting temperature is consistent with that expected for CCB, but a melt for N$_\alpha$CP is not observed at all. The same thermal behavior is observed for the other dopants that have been examined (N$_\alpha$CB, TCP, SCP). The level of dopant does not make a significant difference either, with the same thermal behavior being observed for doping levels of 10−50%. At doping levels above 50%, the T_g became characteristic of the dopant.

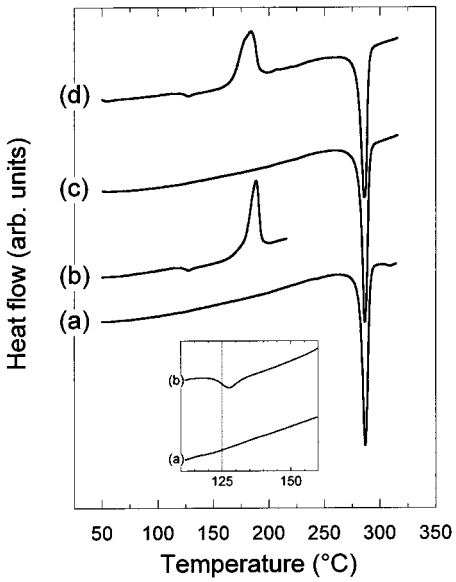


Figure 2. DSC curves for SCB at scan rates of 20 °C/min. (a) The first run shows only crystalline behavior with a melt transition (T_m) at 290 °C. (b) Upon cooling and reheating, the second run displays a glass transition (T_g) at 125 °C along with a crystallization (T_c) at 185 °C. (c) The second run was stopped before the sample was melted; therefore, the third heating cycle only shows crystalline behavior (similar to the first run) with only a melt transition. (d) The fourth heating cycle shows that after the sample has been melted then cooled, it forms a glass with the characteristic T_g. The insert shows expanded scans of (a) and (b) to show the characteristic T_g thermal transition.

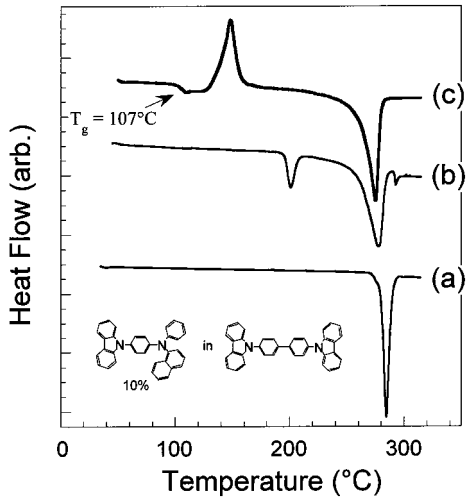


Figure 3. DSC curves (at scan rates of 20 °C/min) for (a) pure CCB. (b) The first run of 10% N_αCP doped into CCB shows the characteristic melts of the two compounds with no glass transition. (c) The second run of 10% N_αCP doped into CCB shows a glass transition at 107 °C, much higher than that of pure N_αCP.

Electrochemistry. In a single heterostructure OLED, holes are carried to the organic interface by the HTL and electrons are carried to the interface by the ETL. For efficient hole/electron recombination, either holes must be injected from the HTL into the ETL or electrons injected into the HTL. To have efficient hole injection from the HTL into the ETL, the energies of the HOMO levels of the two materials must be similar or the HOMO level of the HTL should be below that of the ETL. If the HOMO level of the HTL is above that

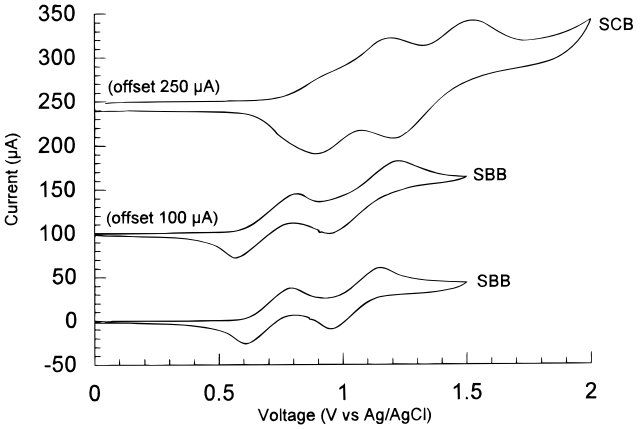


Figure 4. Cyclic voltammagrams for iminostilbenyl biphenyl derivatives SCB, SBB, and SSB (see Scheme 1) in CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate at scan rates of 0.1 V/s using a Ag/AgCl reference electrode and platinum working and counter electrodes.

of the ETL there will be a barrier to hole injection from the HTL to the ETL. To control the ease of hole injection from the HTL to the ETL it is important to know the relative energies of the HOMO levels of different HTL materials. Estimation of the HOMO energy can be done by a variety of methods, including measuring the ionization potential from films using ultraviolet photoelectron spectroscopy[28] and electrochemical measurements. Both methods only lead to estimations of the HOMO energy, since the HOMO energy at the HTL/ETL interface can be significantly altered by charge transfer at the interface.[28] In this study, we have chosen to use electrochemical methods to estimate the HOMO energies of the diamine hole transporters.

The electrochemical method used here to measure HOMO energies was cyclic voltammetry (CV). CV scans were recorded from vs Ag/AgCl at a scan rate of 0.1 V/s, with 0.1 M tetrabutylammonium hexafluorophosphate electrolyte in dry, degassed methylene chloride. For our initial experiments, ferrocene was used as an internal reference for calibration.[29] We found, however, that the measured oxidation potentials varied as much as 0.15 V from those measurements in the absence of ferrocene. We concluded that there were adverse reactions between our diamines and ferrocene and therefore excluded it from all of the measurements reported here and quote our numbers relative to the Ag/AgCl reference. Each of the diamine compounds exhibits two sequential oxidation processes. The potentials for the first oxidation process of each compound are listed in Tables 1 and 2. The first oxidation process is the one that is expected to be involved in hole transport and transfer to the ETL.

Cyclic voltammetry plots shown in Figure 4 for three compounds in the iminostilbene biphenyl series display three typical curves observed for the diamine compounds. The asymmetric (SBB) and the symmetric (SSB) compounds both exhibit ideal reversible redox

(28) Rajagopal, A.; Kahn, A. *Adv. Mater.* **1998**, *10*, 140 and references therein. Rajagopal, A.; Kahn, A. *J. Appl. Phys.*, in press. Seki, K.; Ito, E.; Ishii, H. *Synth. Met.* **1997**, *91*, 137−142 and references therein.

(29) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 462.

behavior with two 1-electron oxidation processes followed by symmetric reduction peaks. These observations are representative for all of the diamines prepared excluding those containing carbazole. The oxidation peaks for the carbazole derivatives (e.g., SCB) are quite broad, and there is a larger voltage difference between the oxidation and the reduction waves than seen for the previous examples. These processes are not diffusion limited and are likely irreversible. This is possibly due to instability of the oxidized carbazole species, which results in degradation of the compound in solution.

A number of general trends can be observed in the oxidation potentials listed in Tables 1 and 2. First, all of the compounds (excluding the carbazoles) containing a phenyl bridge have significantly lower oxidation potentials than the corresponding biphenyl derivatives (on average 0.24 V difference). This is easily understood on the basis of the structures of the phenylene and biphenylene groups. Two amine groups can readily communicate through a phenylene group, while the twist between the phenyl groups in the biphenyl linkage effectively breaks conjugation and lessens the interaction between the amine groups. There is also a general trend from low to high oxidation potentials from the derivatives containing iminodibenzyl (B), iminostilbene (S), phenyl-*m*-tolylamine (T), diphenylamine (D), and 1/2-naphthylphenylamine (N_α/N_β) to carbazole (C). This is true for all of the phenyl derivatives (excluding the carbazole derivatives) across each row (or down the columns) and is generally true for most of the biphenyls. This trend can be explained by the relative electron-withdrawing ability of the arenes to the nitrogen. Derivatives with good electron-donating groups on the arenes, such as iminodibenzyl, yield a relatively higher electron density on the nitrogen atoms that in turn allow it to be more easily oxidized. The carbazole derivatives have markedly higher oxidation potentials than all of the others regardless of the amine on the other side. This suggests that the charge of the oxidized species is not localized on one of the nitrogen atoms but is delocalized over the entire molecule.

Although the electrochemical data do not yield exact HOMO levels, we can observe trends and compare the oxidation potentials to well-understood HTL materials with similar structures HTL materials.[30] We may be able to explain the observed device characteristics on the basis of the expected HOMO energies and predict what compounds will give the best device performance by supplying the best matches in energy to hole injection and ETL layers.

Electronic Structure. All of the diamines examined here are white or yellow solids. The λ_{max} values for their absorption spectra in $CHCl_3$ fall between 250 and 350 nm (Tables 1 and 2). The majority of the compounds show small Stokes shifts between the absorption and emission bands (typically 3000−6000 cm^{-1}), leading to violet to blue emission (λ_{max} = 380−410 nm). We have examined these materials using semiempirical theoretical methods (with the intermediate neglect of differential overlap method, energies and oscillator strength based on CI calculations involving 10 filled and 10 vacant orbitals).[31] These calculations suggest that for most of the molecules in Table the lowest energy electronic transition is largely due to electron transfer from a nitrogen lone pair to the π^* orbital of the biphenyl group. The calculation predicts that this transition should have a high oscillator strength, consistent with the observed spectra, which have measured extinction coefficients of 10^4 Mcm.

For most of the compounds containing an iminostilbene donor, a moderately low energy band is observed in the emission spectrum at 507−518 nm in addition to the violet/blue emission band. For the symmetric diamine (SSB), the band at 530 nm is the only emission band. For the other iminostilbene-containing molecules, the band above 500 nm is a shoulder and the 380−410 nm band is the strong band. Molecular orbital calculations suggest that the lowest energy electronic transitions in these materials do not involve the biphenyl π system but involve electron transfer from the amine nitrogen to the π^* system of the stilbene. A nitrogen to biphenyl π^* transition is also present in the asymmetric materials, at higher energies, with significantly higher oscillator strengths. There are several possible explanations for the large Stokes shift in SSB. Emission from an SSB excimer would lead to significantly red-shifted emission; however, dilution studies show the same emission spectrum at high levels of dilution, precluding excimer or aggregate state emission. If the molecule crosses over to a triplet excited state that could also lead to a significant red shift in emission. The photoluminescent lifetimes for these materials are not consistent with triplet emission. The lifetime for SSB in $CHCl_3$ solution is 6 ns, consistent with singlet emission. The asymmetric iminostilbene biphenyl derivatives (SCB, $SN_\alpha B$, $SN_\beta B$, SDB, STB, SBB) have emission lifetimes for the blue/violet band (380−410 nm) ranging from 1.5 to 3 ns and lifetimes for the green band of 5.5−6.5 ns. The lifetimes for the violet/blue band in these asymmetric derivatives are consistent with the other diamines, whose transitions are associated with nitrogen to biphenyl π^* transitions. The green band only occurs in the iminostilbene derivatives and is most likely due to transition within the iminostilbene group. The large Stokes shift in these materials is not due to excimer or triplet states. A logical proposal for the origin of the large Stokes shift in these materials is that the intense absorption in the ultraviolet is not related to iminostilbene emission. The absorption band for the iminostilbene moiety would be close to 500 nm and may be overshadowed by the intense N to biphenyl π^* band. The excitation spectra of the iminostilbene materials support this conclusion. The excitation spectra of the iminostilbene compounds show an intense band below 400 nm, as expected based on the absorption spectra, and a weak band centered between 450 and 500 nm.

Conclusions

This systematic study of triaryldiamines has supplied some very practical information as to what types of

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(31) Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* 1986, 25, 2728. Anderson, W. P.; Cundari, T. R.; Drago, R. S.; Zerner, M. C. *Inorg. Chem.* **1990**, *29*, 1. Kotzian, M.; Rosch, N.; Schroeder, H.; Zerner, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 7687. ZINDO was run on a Silicon Graphics, Indigo-2 workstation, using Biosym International software.

materials should perform well as HTLs in OLEDs. By varying the arylamines, we have shown which amines in general yield the best thermal stability. The iminostilbene and iminodibenzyl derivatives consistently give higher T_g values than any of the other amines. Electrochemical and spectroscopic measurements give a good picture of the relative HOMO levels and energy gaps for these materials, which are important parameters in the design of efficient OLEDs. In this way, an HTL can be tailored to suit the device application. The asymmetric compounds show enhanced thermal stability over those of the symmetric derivatives due to their ability to form stable glasses and preventing crystallization. For many of these compounds, these thermal enhancements have not hindered but have improved the desired properties exhibited by TPD. We are currently investigating the transport properties of these materials and their use as HTLs in OLEDs.

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Supporting Information Available: Photoluminescence spectra and lifetimes for SSB, SCB, $SN_{\alpha}B$, $SN_{\beta}B$ SDB, STB, SBB, as described in the text (2 pages). Ordering information is given on any current masthead page.

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