

A New Efficient Convergent Synthesis of Conjugated Aryl-containing Dendrimers

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Dendrimers are branched macromolecules that consist of a core, one or more dendrons, and surface groups. Due to their controlled mass, uniform structure, surface functionality and good solubility (relative to linear polymers), they have been studied for a wide range of pharmaceutical applications including solubility enhancement,^{1,2} drug delivery,^{3,4} MRI contrast agents,^{5,6} neutron capture therapy,⁷ gene therapy⁸ and photodynamic therapy.⁹ At the same time, conjugated dendrimers have recently attracted special attention for their potential use in organic light emitting diodes, either as light emitting or charge-transporting layers.^{10,11}

The unique structure of dendrimers allowed for better and more flexible control of their properties. The fact that different parts of dendrimer structure can have different functions allows for independent optimization of the electronic and processing properties. For example, the core in dendrimer can be selected to give the desired luminescence color, while the surface groups could be controlled to give the desired solubility.¹⁰ Despite the large amount of research focused at dendrimers and the large number of prospects for their potential uses, very few dendrimer-based products have reached an industrial development stage. Among the reasons for the slow progress in this area are the multi-step synthetic routes commonly employed for the synthesis of dendrimers and the purification processes required to remove the excess of reagents and byproducts at each generation build-up. Accordingly, much effort have been devoted to develop synthetic methodologies that either follow a growing pattern from a multivalent core in an interactive sequence (divergent), or a dendron is grafted on to the core (convergent). Some progress has been made in this regard, including the polyamidoamine (PAMAM) dendrimers reported by Tomalia,¹² phosphorus-containing dendrimers by Majoral and co-workers,¹³ aliphatic polyester dendrimers by Fréchet and co-workers,¹⁴ and the 3,5-dihydroxybenzyl alcohol based dendrimers by Bourrier and Kakkar.¹⁵ A number of click chemistry protocols have been also applied recently for the preparation of dendrimers, employing Diels-Alder reaction,¹⁶ thiol-ene reactions¹⁷ and azide-alkyne reactions.^{18,19} However, there are still needs to make these processes viable for industrial scale applications.

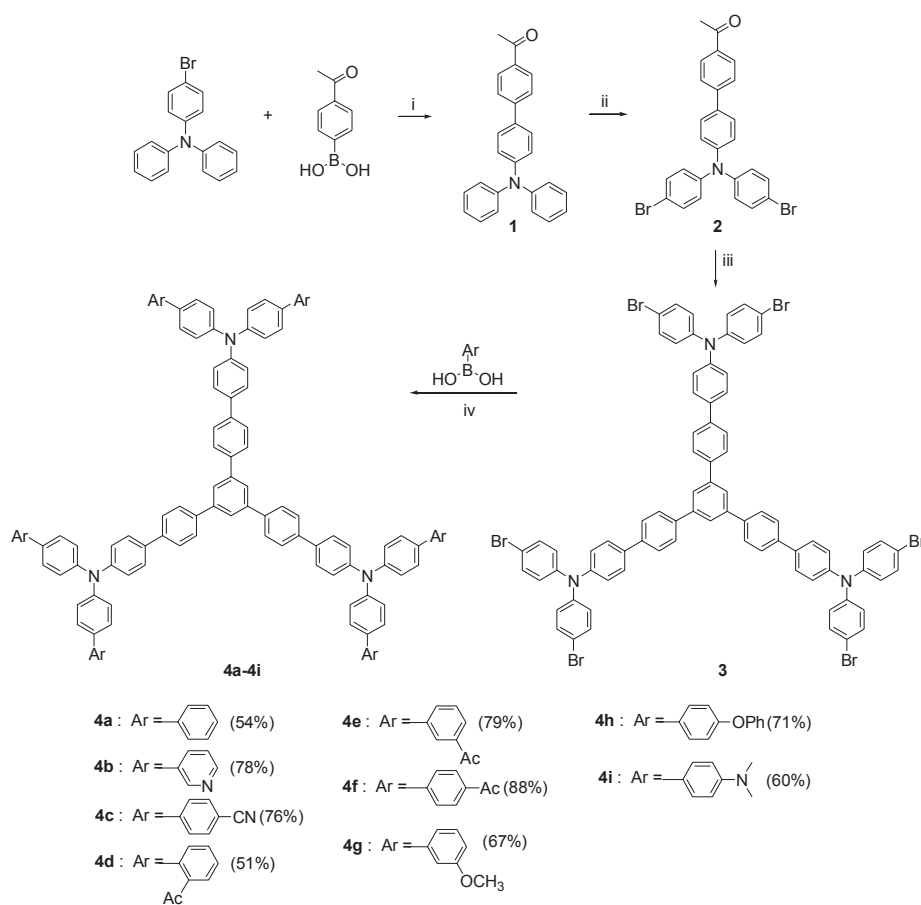
Herein we describe a new convergent synthesis of conjugated dendrimers starting with acetyl substituted dendrons which were dehydrated under the effect of tetrachlorosilane to form a 1,3,5-trisubstituted phenyl core carrying three branches (dendrons) in a star shaped dendrimer.²⁰ This resulted dendrimer

was then subjected to a series of divergent Suzuki couplings for functionalization of the final dendrimers with different groups.²¹ The synthetic protocol is simple and could be easily modified to obtain either conjugated or saturated dendrimers bearing variable groups. The products obtained in each preparation step are easily purified by simple crystallization, making the process easily applicable at larger industrial scale.

As shown in Scheme 1, the synthesis of the key dendron **2** started by the Suzuki coupling of 4-bromotriphenylamine with 4-acetylphenylboronic acid under the catalysis of dichlorobis(triphenylphosphine)Pd(II) and in the presence of sodium carbonate in a mixed solvent of acetonitrile and water in a (1:1, v/v) ratio. The resulted highly green luminescent acetyl intermediate **1** was obtained in a good yield of 76%, and was then subjected to *p*-phenyl bromination under the effect of *N*-bromosuccinimide in DMF to yield the target dibromoacetyl-dendron **2** in 97% yield. Every three moles of the key dendron **2** were then dehydrated at the acetyl-moiety terminal part under the effect of excess tetrachlorosilane to yield the hexabromo intermediate dendrimer **3** in a 72% yield. This intermediate dendrimer **3** was then subjected to a series of Suzuki coupling reactions with a number of phenyl boronic acids in the presence of dichlorobis(triphenylphosphine)Pd(II) and potassium carbonate in a mixed solvent of THF/water in a (4:1, v/v) ratio to yield the final target dendrimers **4a-i** in moderate to good yields.

In order to get a more clear picture about the effect of substitution at these new conjugated dendrimers on their photophysical properties, the absorption and photoluminescence (PL) spectra of compounds **4a-i** were recorded in dichloromethane using UV-vis. and luminescence spectroscopy, respectively. The results are shown in Table 1 and the typical spectra are shown in Figure 1.

As shown in Figure 1, the UV spectra of all the recorded compounds showed absorption maxima in the range of (350 - 380 nm). Excitation of these compounds by a single beam UV light at the λ_{max} of their absorption spectra resulted in an intense emission at the range of (450 - 510 nm) at a very low concentration of 10 nM. By correlating between compounds structures and the intensity of photoluminescence, we found that the substitution with an electron deficient heterocyclic system like the pyridine ring in **4b** reduced the luminescence intensity. The *m*-substitution pattern (as in **4e** and **4g**) was found also to be unfavored for good luminescence. However, the *p*-substitution (as in **4f**) remains to be the best for the highest luminescence.



Reaction conditions and yields: (i) Pd(PPh₃)₂Cl₂, Na₂CO₃, N₂, CH₃CN/H₂O (1:1, v/v), 80 °C, 3 h, 76% (ii) NBS, DMF, 60 °C, 18 h, 97% (iii) SiCl₄, EtOH/toluene (5:1, v/v), reflux, 24 h, 72% (iv) Pd(PPh₃)₃Cl₂, K₂CO₃, N₂, THF/H₂O (4:1), 80 °C, 24 h.

Scheme 1. Synthetic pathway for dendrimers **4a-i** and reaction conditions

Table 1. The absorption and luminescence maxima of the compounds **4a-i**

Compound	λ_{\max} (nm)		FWHM ^c (nm)
	UV ^a	PL ^b	
4a	353	468	87
4b	355	489	115
4c	371	484	78
4d	354	503	85
4e	358	501	101
4f	373	508	91
4g	355	459	70
4h	355	491	91
4i	358	500	91

^ameasured in CH₂Cl₂ solution at 5 μ M concentration, ^brecorded by single beam excitation in CH₂Cl₂ solution at 10 nM concentration, ^cThe full widths at half maximum value.

In summary, we have designed a new simple and efficient convergent synthetic protocol for the preparation of conjugated dendrimers. The synthetic pathway could be modified easily for the preparation of different conjugated and saturated suitably substituted dendrimers for variable applications. The synthetic advantages and the ease of purification by simple crystalliza-

tion allows for the large scale application of this synthetic protocol at the industrial scale.

Experimental Section

General. ¹H-NMR (300 MHz) and ¹³C-NMR (75 MHz) were recorded on a Bruker Avance 300 spectrometer with TMS as an internal reference. The IR spectra were recorded on Perkin Elmer Spectrum GX spectrometer. Melting points were taken on a Thomas-Hoover capillary melting apparatus and were uncorrected. UV-visible spectra and luminescence spectra were recorded on S-2130 spectroscopy and RF-5301-PC luminescent spectroscopy, respectively. Column chromatography was performed on Merck silica gel 60 (230 - 400 mesh). TLC was carried out using glass sheets precoated with silica gel 60 F254 prepared by E. Merck. All the commercially available reagents were obtained from Aldrich and Tokyo Kasei Chemical and generally used without further purification.

1-(4'-Diphenylaminobiphenyl-4-yl)ethanone (1): A mixture of 4-bromotriphenylamine (2.0 g, 6.17 mmol), 4-acetylphenylboronic acid (1.12 g, 6.80 mmol), dichlorobis(triphenylphosphine)Pd(II) (130 mg, 0.19 mmol) and Na₂CO₃ (460 mg, 4.32 mmol) was stirred in a mixture of acetonitrile and water (1:1, v/v, 80 mL). N₂ gas was bubbled into this mixture for 10 min,

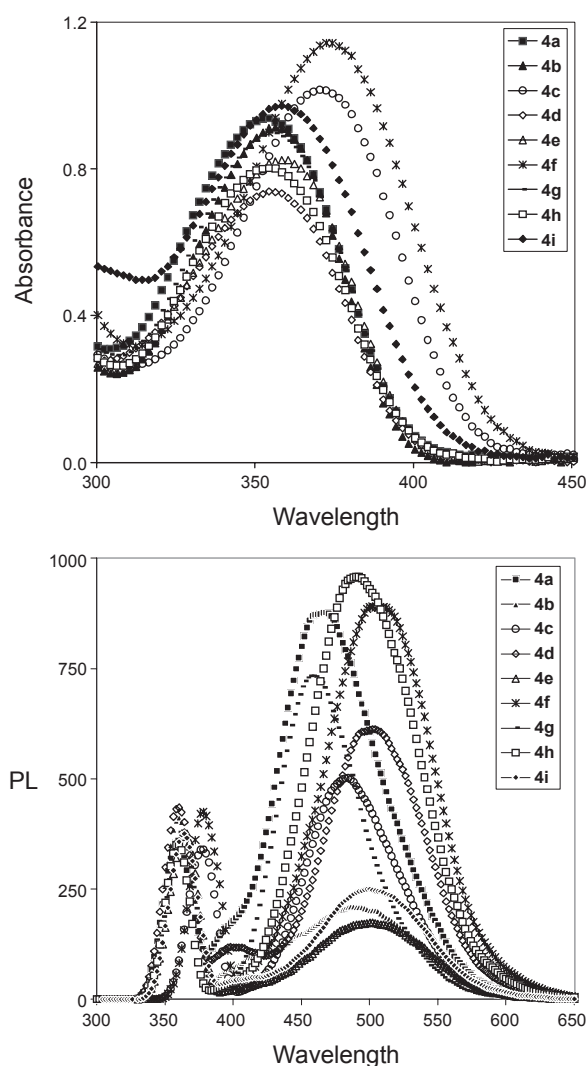


Figure 1. UV(upper panel) and PL(lower panel) spectra for compounds **4a-i**.

and then the mixture was heated at 80 °C while stirring under N₂ atmosphere for 3 h. The reaction mixture was left to cool at room temperature, poured into ice water (80 mL), and then extracted with methylene chloride (150 mL × 3). The organic layer was separated, dried over anhydrous MgSO₄, and then evaporated under vacuum to yield the crude product which was then purified by flash chromatography (silica gel, hexane : EtOAc = 6 : 1, v/v) to give **1** (1.7 g, 76% yield) as bright green powder. mp 97 - 98 °C; IR (KBr) ν 1679, 1590, 1489, 1268, 821, 750, 697 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 2.65 (s, 3H), 7.08 (t, J = 7.3 Hz, 2H), 7.15-7.33 (m, 10H), 7.53 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 8.03 (d, J = 8.1 Hz, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 26.64, 123.29, 123.37, 124.79, 126.50, 127.93, 128.98, 129.39, 133.12, 135.32, 145.22, 147.42, 148.19, 197.71.

1-(4'-(*N,N*-Bis(4-bromophenyl)amino)biphenyl-4-yl)ethanone (2**):** A mixture of compound **1** (1.5 g, 4.13 mmol) and *N*-bromosuccinimide (1.55 g, 8.67 mmol) was stirred in DMF (10 mL) at room temperature for 1 h, then heated at 60 °C for 18 h. The reaction mixture was left to cool, then poured over

brine solution containing ice (200 mL). The resulted precipitate was filtered, washed with cold water, dried, and then crystallized from ethylacetate to yield pure **2** (1.85 g, 97% yield) as yellow crystals. mp 181 - 182 °C; IR (KBr) ν 1680, 1602, 1486, 1313, 1286, 1266, 820 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 2.65 (s, 3H), 7.01 (d, J = 8.8 Hz, 4H), 7.14 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.8 Hz, 4H), 7.54 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.4 Hz, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 26.65, 116.14, 124.00, 125.93, 126.64, 128.25, 129.01, 132.54, 134.44, 135.59, 144.66, 146.15, 147.15, 197.63.

1,3,5-Tris(4'-(*N,N*-bis(4-bromophenyl)amino)biphenyl-4-yl)benzene (3**):** To a stirred suspension of **2** (1.5 g, 2.88 mmol) in a mixture of abs. ethanol and dry toluene (5:1, v/v, 30 mL) was added silicon tetrachloride (6.6 mL, 57.6 mmol) dropwise under N₂ atmosphere. The reaction temperature was raised to reflux, and the mixture was heated under N₂ for 24 h. The reaction mixture was left to cool, and the resulted green precipitate was filtered, washed with cold ethanol, and crystallized from chloroform/ethanol mixture, to yield pure **3** (1.1 g, 72% yield) as yellowish green crystals. mp > 300 °C; IR (KBr) ν 1578, 1483, 1312, 1270, 1070, 1005, 817, 511 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.02 (d, J = 8.7 Hz, 12H), 7.15 (d, J = 8.4 Hz, 6H), 7.39 (d, J = 8.7 Hz, 12H), 7.57 (d, J = 8.5 Hz, 6H), 7.71 (d, J = 8.1 Hz, 6H), 7.80 (d, J = 8.2 Hz, 6H), 7.89 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 115.80, 124.43, 124.90, 125.70, 127.18, 127.77, 128.02, 132.27, 132.47, 135.57, 139.63, 139.74, 141.94, 146.34.

General procedure for the synthesis of compounds 4a-4i. A mixture of compound **3** (200 mg, 0.13 mmol), the appropriate aryl boronic acid derivative (1.06 mmol), dichlorobis(triphenylphosphine)Pd(II) (28 mg, 0.04 mmol) and K₂CO₃ (110 mg, 0.80 mmol) was stirred in a mixture of THF and water (4:1, v/v, 10 mL). N₂ gas was bubbled into this mixture for 10 min, and then the mixture was heated at 80 °C while stirring under N₂ atmosphere for 24 h. The reaction mixture was left to cool at room temperature, poured into brine solution (50 mL), and then extracted with methylene chloride (100 mL × 3). The organic layer was separated, dried over anhydrous MgSO₄, and then evaporated under vacuum to yield the crude product which was then purified by crystallization from the appropriate solvent.

1,3,5-Tris(4'-(*N,N*-bis(biphenyl-4-yl)amino)biphenyl-4-yl)benzene (4a**):** It was obtained from toluene as light brown powder (107 mg, 54% yield); mp 207 - 208 °C; IR (KBr) ν 1599, 1517, 1485, 1321, 1292, 817, 763, 696 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.03-7.33 (m, 18H), 7.39 (d, J = 6.9 Hz, 6H), 7.47-7.52 (m, 12H), 7.59-7.67 (m, 30H), 7.78 (d, J = 7.6 Hz, 6H), 7.85 (d, J = 7.6 Hz, 6H), 7.95 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 124.38, 124.53, 125.70, 126.74, 126.95, 127.14, 127.75, 127.85, 127.96, 128.80, 134.91, 135.74, 139.86, 140.59, 141.98, 146.80, 147.03; UV λ_{\max} = 353 nm (CH₂Cl₂); PL λ_{\max} = 468 nm (CH₂Cl₂).

1,3,5-Tris(4'-(*N,N*-bis(4-(pyridin-3-yl)phenyl)amino)biphenyl-4-yl)benzene (4b**):** It was obtained from DMSO as buff powder (155 mg, 78% yield); mp 239 - 240 °C; IR (KBr) ν 1599, 1513, 1496, 1474, 1322, 1291, 1269, 817, 801, 710, 557 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.29-7.39 (m, 24H), 7.54 (d, J = 7.9 Hz, 12H), 7.63 (d, J = 7.8 Hz, 6H), 7.74 (d, J = 7.6 Hz, 6H), 7.82 (d, J = 7.6 Hz, 6H), 7.87-7.91 (m, 9H), 8.59 (d, J = 2.6 Hz, 6H), 8.88 (s, 6H); UV λ_{\max} = 355 nm (CH₂Cl₂); PL

λ_{\max} = 489 nm (CH₂Cl₂).

1,3,5-Tris(4'-(N,N-bis(4'-cyanobiphenyl-4-yl)amino)biphenyl-4-yl)benzene (4c): It was obtained from DMSO as greenish yellow powder (166 mg, 76% yield); mp 250 - 252 °C; IR (KBr) ν 2226, 1596, 1493, 1324, 1292, 1184, 817, 533 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.28 (d, J = 8.7 Hz, 18H), 7.56 (d, J = 8.6 Hz, 12H), 7.63-7.77 (m, 36H), 7.83 (d, J = 8.1 Hz, 6H), 7.91 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 110.45, 119.05, 124.33, 124.93, 125.30, 127.11, 127.24, 127.81, 128.10, 128.21, 132.68, 133.50, 135.99, 139.65, 139.80, 141.95, 144.82, 146.34, 147.78; UV λ_{\max} = 371 nm (CH₂Cl₂); PL λ_{\max} = 484 nm (CH₂Cl₂).

1,3,5-Tris(4'-(N,N-bis(2'-acetyl)biphenyl-4-yl)amino)biphenyl-4-yl)benzene (4d): It was purified by flash chromatography (silica gel, hexane : EtOAc = 1 : 1, v/v) to afforded the target compound as golden yellow powder (118 mg, 51% yield); mp 161 - 162 °C; IR (KBr) ν 1686, 1599, 1509, 1496, 1474, 1321, 1266, 1232, 817, 761 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 2.19 (s, 18H), 7.25-7.67 (m, 60H), 7.76 (d, J = 8.1 Hz, 6H), 7.85 (d, J = 8.0 Hz, 6H), 7.94 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 30.54, 124.06, 125.03, 127.25, 127.31, 127.82, 127.98, 128.10, 129.99, 130.14, 130.84, 132.06, 132.19, 135.25, 135.68, 139.74, 140.08, 140.88, 141.99, 146.61, 147.18, 204.91; UV λ_{\max} = 354 nm (CH₂Cl₂); PL λ_{\max} = 503 nm (CH₂Cl₂).

1,3,5-Tris(4'-(N,N-bis(3'-acetyl)biphenyl-4-yl)amino)biphenyl-4-yl)benzene (4e): It was obtained from toluene as yellow powder (183 mg, 79% yield); mp 176 - 178 °C; IR (KBr) ν 1685, 1599, 1514, 1496, 1479, 1323, 1295, 1236, 818, 795, 693 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 2.68 (s, 18H), 7.29 (d, J = 8.7 Hz, 18H), 7.51-7.64 (m, 24H), 7.74 (d, J = 8.2 Hz, 6H), 7.81 (d, J = 7.7 Hz, 12H), 7.90-7.94 (m, 9H), 8.22 (s, 6H); ¹³C-NMR (75 MHz, CDCl₃) δ 26.77, 124.51, 124.70, 124.87, 126.47, 126.93, 127.16, 127.77, 127.95, 128.10, 129.10, 131.26, 134.69, 135.35, 137.71, 139.68, 139.74, 141.07, 141.95, 146.75, 147.21, 198.09; UV λ_{\max} = 358 nm (CH₂Cl₂); PL λ_{\max} = 501 nm (CH₂Cl₂).

1,3,5-Tris(4'-(N,N-bis(4'-acetyl)biphenyl-4-yl)amino)biphenyl-4-yl)benzene (4f): It was obtained from toluene as orange powder (205 mg, 88% yield); mp 255 - 257 °C; IR (KBr) ν 1682, 1596, 1522, 1493, 1324, 1268, 817, 598 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 2.65 (s, 18H), 7.28 (d, J = 7.6 Hz, 18H), 7.58-7.75 (m, 36H), 7.81 (d, J = 8.0 Hz, 6H), 7.90 (s, 3H), 8.04 (d, J = 8.1 Hz, 12H); ¹³C-NMR (75 MHz, CDCl₃) δ 26.70, 124.35, 125.03, 126.62, 127.20, 127.79, 128.01, 128.20, 129.05, 134.20, 135.49, 135.64, 139.71, 141.94, 144.99, 146.52, 147.50, 197.73; UV λ_{\max} = 373 nm (CH₂Cl₂); PL λ_{\max} = 508 nm (CH₂Cl₂).

1,3,5-Tris(4'-(N,N-bis(3'-methoxy)biphenyl-4-yl)amino)biphenyl-4-yl)benzene (4g): It was obtained from DMSO as dark green powder (150 mg, 67% yield); mp 178 - 179 °C; IR (KBr) ν 1599, 1514, 1479, 1320, 1293, 1212, 817, 777, 694, 532 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 3.89 (s, 18H), 6.90 (d, J = 8.0 Hz, 6H), 7.17-7.28 (m, 30H), 7.37 (t, J = 7.9 Hz, 6H), 7.55 (d, J = 8.5 Hz, 12H), 7.61 (d, J = 8.4 Hz, 6H), 7.73 (d, J = 8.1 Hz, 6H), 7.81 (d, J = 8.1 Hz, 6H), 7.90 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 55.33, 112.32, 112.47, 119.30, 124.47, 124.87, 127.15, 127.76, 127.88, 128.04, 129.83, 134.95, 135.54, 139.59, 139.81, 141.98, 142.12, 146.91, 146.96, 159.98; UV λ_{\max} = 355 nm (CH₂Cl₂);

PL λ_{\max} = 495 nm (CH₂Cl₂).

1,3,5-Tris(4'-(N,N-bis(4'-phenoxy)biphenyl-4-yl)amino)biphenyl-4-yl)benzene (4h): It was obtained from DMSO as dark green powder (193 mg, 71% yield); mp 196 - 198 °C; IR (KBr) ν 1589, 1486, 1322, 1238, 1167, 870, 818, 751, 692, 519 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.09-7.28 (m, 48H), 7.39 (t, J = 7.6 Hz, 12H), 7.52-7.63 (m, 30H), 7.74 (d, J = 7.7 Hz, 6H), 7.83 (d, J = 8.1 Hz, 6H), 7.91 (s, 3H); UV λ_{\max} = 355 nm (CH₂Cl₂); PL λ_{\max} = 491 nm (CH₂Cl₂).

1,3,5-Tris(4'-(N,N-bis(4'-(N,N-dimethylamino)biphenyl-4-yl)amino)biphenyl-4-yl)benzene (4i): It was obtained from toluene as orange powder (140 mg, 60% yield); mp > 300 °C; IR (KBr) ν 3474, 1609, 1497, 1320, 811 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 3.01 (s, 36H), 6.83 (d, J = 7.0 Hz, 12H), 7.16-7.24 (m, 18H), 7.49-7.60 (m, 30H), 7.72 (d, J = 7.9 Hz, 6H), 7.80 (d, J = 7.9 Hz, 6H), 7.90 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 40.87, 113.23, 123.72, 124.11, 124.74, 125.02, 125.37, 127.04, 127.38, 127.70, 127.85, 132.25, 134.19, 135.75, 139.42, 139.93, 141.99, 145.78, 146.82, 147.30; UV λ_{\max} = 358 nm (CH₂Cl₂); PL λ_{\max} = 500 nm (CH₂Cl₂).

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