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Photoactive amorphous molecular materials based on quinoline amines and their synthesis by Friedländer condensation reaction

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ABSTRACT

A new class of conjugated quinoline amines was prepared by Friedländer condensation reaction. They showed stable amorphous state below glass transition temperatures as examined by differential scanning calorimetry and X-ray diffraction studies. Additionally, they exhibited fluorescence properties in the blue to green region of visible spectrum in both solution and solid state. Their fluorescence quantum efficiencies in chloroform were in a broad range of 3–45%. Interestingly, they formed stable fibers with micrometer thickness drawn from melt, which were characterized by polarizing optical microscopy and scanning electron microscopy studies.

1. Introduction

Since the discovery of fluorescent compounds, they have found applications as fluorophores, used for the detection of cell membranes, proteins and DNA,[1] sensors for heavy metals,[2] and most recently as light-emitting layers in organic semiconductors.[3] To make fluorescent compounds appropriate for these diverse applications different requirements must be met. Above all, their high-quantum yields are one of the most desirable properties. The amorphous molecular materials have attracted unabated attention as materials for optoelectronic devices as hole transporting/blocking, electron transporting/blocking and ambipolar layers. Amorphous state is advantageous over crystalline, polycrystalline or liquid-crystalline states since it is easier to produce a film, it is transparent, and it has homogeneous properties. Amorphous polymers are also well-known, but they are polydispersed, in many cases, difficult to purify, characterize, and process. It is a challenging task to synthesize amorphous molecular materials that are capable of forming into stable glasses below their glass transition temperatures (T_g), since small molecules have a natural tendency to crystallize; therefore, they have to possess certain structural irregularities in their chemical architectures. The general factor necessary to prevent crystallization is to use large rigid structures with bulky substituents, which cause non-planarity. Even though this design is met with some success, in many cases, rapid cooling processes from their melts are required to prevent molecules from producing high-ordered crystalline states. While forced to attain glassy states via cooling processes, such films often tend to crystallize over time, which could severely limit their potential.[4] Additionally, the method is known as vapor deposition that can be applied to organic compounds to produce amorphous phase with extraordinary thermodynamic and kinetic stability, and high density. Its stability is optimized when deposition occurs on a substrate at a temperature of 50 K below its T_g.[5]

To overcome these disadvantages we designed a novel class of quinoline amines as amorphous molecular materials. They are completely conjugated and each of their molecular structures are asymmetric that evidently contributes to its sustaining amorphous state, which is known to favor the amorphous state.[4] Amino groups were added in different positions of the 2-phenyl group: the phenyl group attached at the 2-position of the quinoline moiety. The variation of chemical structures would enable one to study the effect of molecular structures on their thermal transitions as well as tuning of fluorescence properties and optimization of quantum yields.

2. Results and discussion

The Friedländer condensation reaction is a facile synthetic method for preparing quinolines, oligoquinolines, polyquinolines, and polyanthrazolines.[6,7] It has numerous applications as a key step in the total synthesis of many natural products like streptonirin,[8a] camptothecin,[8b] irinotecan,[8c] and nothapodytine B.[8d] To prepare

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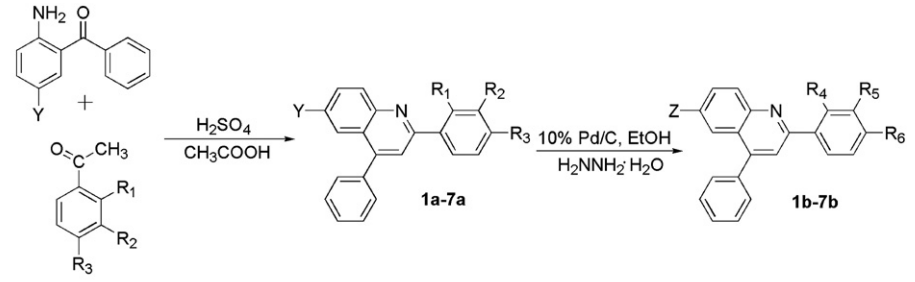
a class of quinoline amines **1b**–**7b**, we used an acid-catalyzed Friedländer condensation reaction followed by hydrogenation with hydrazine monohydrate in presence of Pd/C as shown in Scheme 1.



	Y	R_1	R_2		Yield %
1a	NO_2	H	H		93
2a*	H	H	H	NO_2	85
3a*	H	H	NO_2	H	89
4a	NO_2	H	H	NO_2	87
5a	NO_2	H	NO_2	H	88
6a	NO_2	NO_2	H	H	56
7a	NO_2	H	H	$(CH_2)_5CH_3$	92

	Z	R_4	R_5	R_6	Yield %
1b	NH_2	H	H	H	91
2b	H	H	H	NH_2	48
3b	H	H	NH_2	H	82
4b	NH_2	H	H	NH_2	81
5b	NH_2	H	NH_2	H	88
6b	NH_2	NH_2	H	H	62
7b	NH_2	H	H	$(CH_2)_5CH_3$	76

* prepared with diphenyl phosphate (DPP)

Scheme 1. Synthesis of quinoline amines **1b**–**7b** in two steps.

The thermal properties of quinoline amines **1b**–**7b** are compiled in Table 1. In the first heating cycle, they exhibited notable melting transitions (T_m) of the solvent-induced crystals, ranging from 89 to 194 °C. In the second heating cycles, all of them showed only the T_g. Their amorphous states were presumably related to the presence of asymmetric structural moieties. Both T_g and T_m temperatures were found to be affected by the different substituents. Compounds **1b** and **2b** showed identical T_m and T_g where **3b** had a little lower T_m of 140 °C, and consequently lower T_g of 40 °C since the amino group is in the low-symmetry *meta* position. The three compounds **4b**–**6b** are disubstituted amines as well as isomers of one another. The first substituent is an amino group at position Z and the second substituent is another amino group at positions R_6, R_5, and R_4, respectively. Their thermal transitions were significantly increased; T_m values ranged from 132 to 194 °C, and T_g values ranged from 61 to 90 °C.

Compound **7b** is also a disubstituted amine but has an amino group at position Z and a hexyl group at position **R_6**. It showed the lowest T_m of 89 °C and the lowest T_g at 15 °C. The representative DSC thermograms of compound **4b** are shown in Fig. 1. In the first heating cycle, it exhibited a sharp T_m at 194 °C. After the first heating cycle, it was cooled slowly at a rate 10 °C/min and showed a T_g at 90 °C in the first cooling cycle. Interestingly, its T_g retained in the subsequent cycles without any cold-crystallization: crystallization above the glass transition temperature on heating and crystallization exotherms, demonstrating its stability in the amorphous state. Overall, it has both the highest T_g and T_m among the compounds examined, since it possesses the most symmetrical chemical structure. These thermal properties demonstrated that compounds/glasses **1b**–**7b** are excellent candidates for amorphous molecular materials[4b] for electronic devices and their thermal transitions are tunable with the modifications of their chemical structures. In addition, given their relatively low T_g and T_m temperatures, they are attractive candidates for future studies of molecular dynamics of glassy materials.[9]

The X-ray powder diffraction (XRD) patterns of the compounds in this study further confirm that they can form completely amorphous materials. In Fig. 2 the representative XRD patterns are displayed for comparison of the crystalline and amorphous states of amino quinoline **1b** and diamino quinoline **4b**. The multiple sharp peaks of strong intensities present in Fig. 2a,b are indicative of the highly crystalline nature of these compounds. On the other hand, Fig. 2c,d show broad diffraction peaks with relatively low intensities at both small and wide angles, which are the characteristic features of glassy phases of compounds. These peaks can be assigned to the intermolecular short-range interactions that are parallel and perpendicular to the long axes of the molecules. The *d*-spacing values of **1b** and **4b** obtained from the diffuse peak maxima at small angles by using Bragg's equation are 0.98 and 0.91 nm, respectively, comparable to the molecular lengths ca. 1.1 nm obtained from the MM2 calculation. Meanwhile, the broad wide-angle diffraction peaks indicate an average intermolecular separation of 0.46 and 0.47 nm, respectively, and they are the result

Table 1
Thermal properties of quinoline derivatives **1a**–**7a** and **1b**–**7b**

Compound	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
First heating	210 °C (T_m)	167 °C (T_m)	159 °C (T_m)	282 °C (T_m)	246 °C (T_m)	229 °C (T_m)	133 °C (T_m)
Second heating	210 °C (T_m)	166 °C (T_m)	158 °C (T_m)	282 °C (T_m)	246 °C (T_m)	60 °C (T_g)	133 °C (T_m)
Compound	**1b**	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**
First heating	150 °C (T_m)	150 °C (T_m)	140 °C (T_m)	194 °C (T_m)	192 °C (T_m)	132 °C (T_m)	89 °C (T_m)
Second heating	52 °C (T_g)	52 °C (T_g)	40 °C (T_g)	90 °C (T_g)	76 °C (T_g)	61 °C (T_g)	15 °C (T_g)
T_g/T_m[a]	0.77	0.77	0.76	0.78	0.85	0.82	0.80

[a] Ratio of absolute temperatures (K).[9]

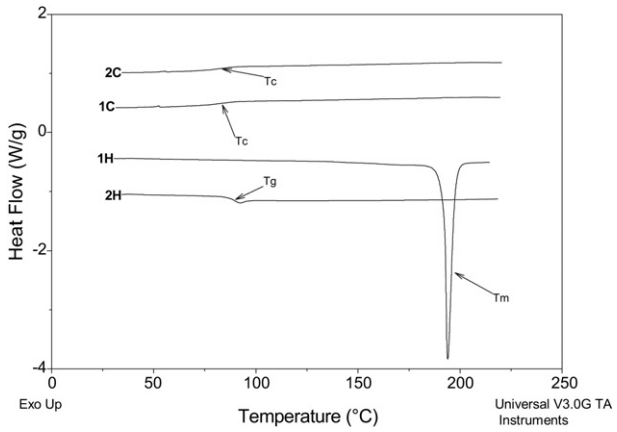


Fig. 1. DSC thermograms of compound **4b** obtained at heating and cooling rates of 10 °C/min in nitrogen.

of π–π stacking of these heterocyclic amine molecules.[10] On melting these compounds between two cover glasses, we were able to form thin amorphous films, which we then examined with polarizing optical microscopy (POM) studies to understand their film morphologies. In all cases, the samples produced uniformly isotropic thin films, which are very similar to many amorphous molecular materials.[4] Remarkably, we successfully drew fibers by pulling their melts with a pair of tweezers with thickness of 60–120 μm, which are visible to the naked eye. The formation of fibers from the melts of heterocyclic amines by self-assembly is quite interesting, since it could be a very useful tool for the construction of compounds that are capable of forming fibers from their nano-sized objects in the burgeoning field of nanotechnology.[11a] To our knowledge, these amines are the first examples of organic compounds that are capable of forming fibers from their melts. This property may be related to the amorphous nature of these compounds that remains to be explored. Note here that in the literature there is one example of a peptidomimetic molecule that undergoes self-assembly forming micro- and nano-fiber in the melt on cooling.[11b] Most fibers, usually produced from the organogels prepared in various solvents including water, reported in the literature can only been seen by POM and scanning electron microcopy (SEM) studies. In some cases, one could be able to pull fibers from the organogel with a pair of tweezers. There are many intermolecular interactions in the formation of organogels some of which include hydrogen bond, hydrophobic and electrostatic association, and van der Waals interactions.[11b–d] Additionally, fibers usually form from the melts and solutions of polymers because of their macromolecular sizes.[12] In this regard, the formation of fibers from organic amines in the melts constitutes a new and promising area of research in nanotechnology. Fig. 3a,b shows photomicrographs of POM and Fig. 6c,d shows SEM images of hand-drawn fibers of **1b** and **4b** from their melts. The morphologies of these fibers were found to be isotropic in nature with very smooth surfaces as examined with both POM and SEM studies. In Fig. 3c the SEM revealed some roughness to the surface of the fiber of compound **1b**, while the cross-section showed its uniform nature. On the other hand, compound **4b**, exhibited much smoother surface than **1b** (Fig. 3d). The cross-section of the compound **4b** demonstrated

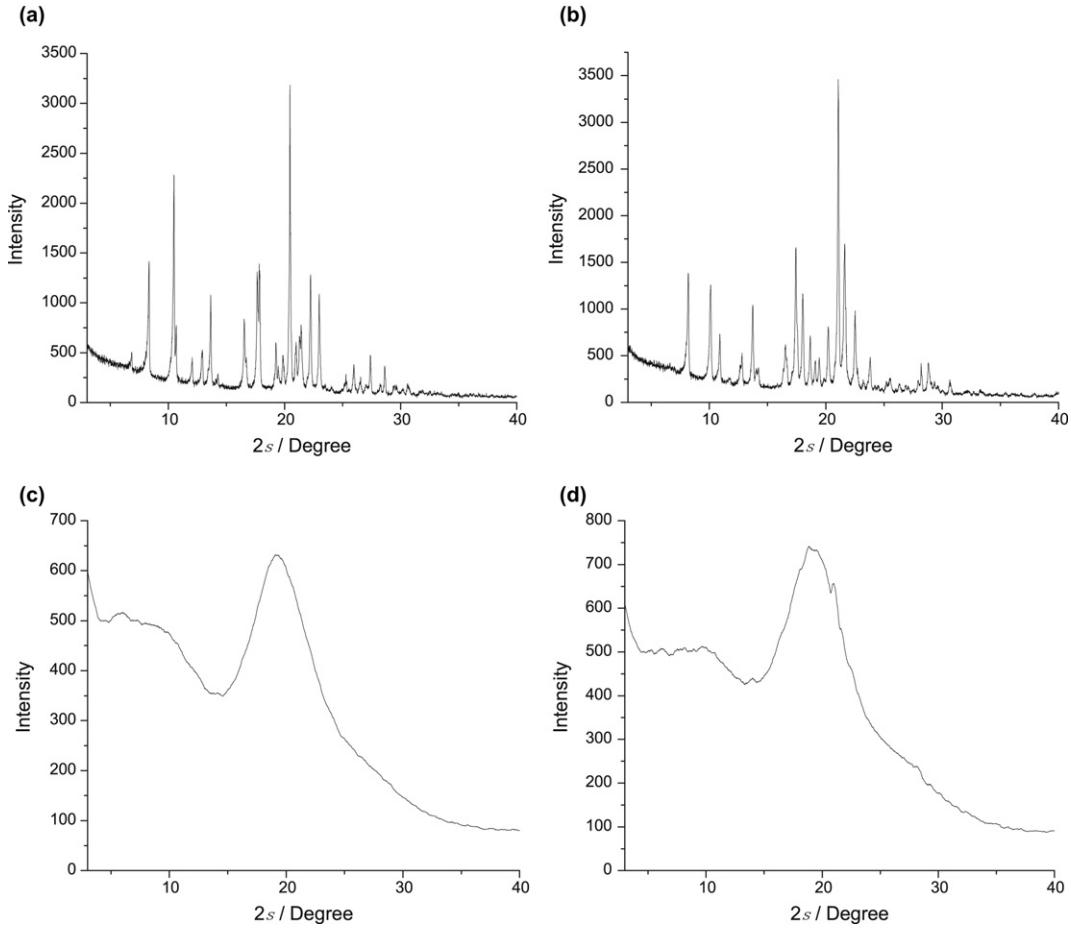


Fig. 2. XRD plots of compounds **1b** and **4b** (a,b) in their crystalline states obtained from solvents recrystallization and (c,d) in their amorphous states prepared from their melts, respectively.

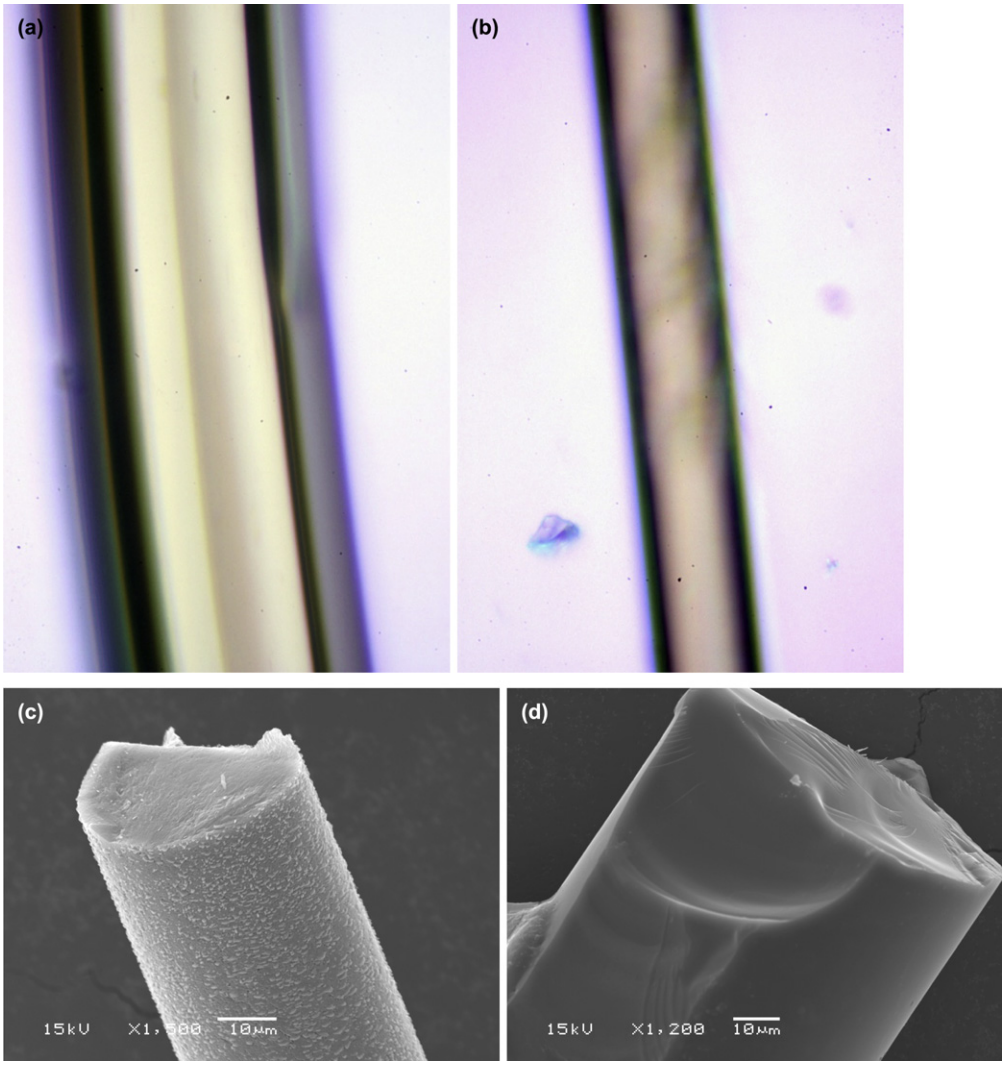


Fig. 3. (a,b) photomicrographs with POM (magnification 400x) and (c,d) images of SEM of hand-drawn fibers from the melts of compounds **1b** and **4b**, respectively.

a similar uniformity as for **1b**. At the present time, it is difficult to speculate the molecular interactions that are involved in the formation of fibers from these compounds in these series.

On one hand, quinine is a naturally occurring compound that exhibits strong fluorescence and, therefore, is usually used as a fluorescent standard.[1] On the other hand, quinoline does not fluoresce at all even though it is structurally similar to quinine, which has two additional substituents. These results convey the concept that substituents have a key effect on the properties of fluorophores. Recently, phase-tunable fluorophores based on benzobis(imidazolium) salts have also been reported in the literature.[13] In our studies we utilized a different type of quinoline moiety and attached substituents in different positions in order to examine how they affect their light emission properties as well as their quantum yields. Optical properties of both UV–vis absorption and photoluminescence including quantum yields[14] of **1b**–**7b** are summarized in Table 2. Since they had excellent solubilities in various organic solvents, their photoluminescence properties were

Table 2
Optical properties of quinoline amines **1b**–**7b**

Compound	**1b**	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**
UV abs $CHCl_3$ (nm)	280, 300sh	290, 420	345	290, 440	300, 420	325, 435, 480	310, 415
PL λ_{em} Toluene (nm)	419	408	412	426	419	426	418
PL λ_{em} $CHCl_3$ (nm)	485	482	417	436	434	426	483
PL λ_{em} THF (nm)	446	452	475	448	444	445	446
PL λ_{em} CH_3OH (nm)	463	491	491	467	461	460	462
PL λ_{em} CH_3CN (nm)	443	478	510	443	448	448	444
PL λ_{em} film (nm)[a]	418, 529	402, 508	404	430	430	—[b]	421, 514
Φ_F (%)[c] $CHCl_3$	45	9	2[d]	31	23	3	32

[a] Film was prepared in a polystyrene matrix cast from $CHCl_3$.
[b] Too weak to measure the light emission.
[c] Quantum yield was determined against diphenylanthracene as standard (Φ_F=0.9) in solution.[10]
[d] Quantum yield was measured in THF.

examined in various solvents having a wide range of polarities. Their photoluminescence spectra in chloroform are displayed in Fig. 4. The wavelengths of light emission range from blue (417 nm) to green (485 nm). Compounds **1b**, **2b**, and **7b** showed distinctive green emission with λ_{em} values at 485, 482, and 483 nm, when excited at 290, 410, and 300 nm, respectively. On the other hand, structurally similar compound **3b** showed a hypsochromically shifted λ_{max} of 417 nm when excited at 300 nm. This large difference was due to the fact that the amino group is *meta* relative to the quinoline moiety. Disubstituted compounds **4b**–**6b** had λ_{em} at 436, 434, and 426 nm when excited at 300, 265, and 350 nm, respectively, showing a slight hypsochromic shift when changing the position of the second amino group from *para*- to *meta*- to *ortho*-. When comparing the optical properties of these compounds, it was found that changing the substituents and their positions had a key effect on their fluorescence behavior. Moreover, their fluorescence properties in various organic solvents also suggested a strong evidence of solvatochromic effect.[1] Taking compound **3b** for instance showed a large bathochromic shift with increasing solvent polarity (Fig. 5a). When examined in low polarity solvent toluene (ϵ=2.4), it showed a major λ_{em} peak at 412 nm when excited at 300 nm whereas in high polarity acetonitrile (ϵ=37.5) a major λ_{em} was observed at 512 nm when excited at 300 nm. The difference between their λ_{max} values was 98 nm, which was due to the more polar excited state than the ground state, which is a positive solvatochromism.[1] On the other hand, examining the optical properties of compound **1b** revealed a more complex behavior (Fig. 5b). A slight change in solvent polarity from toluene (ϵ=2.4) to $CHCl_3$ (ϵ=5.5), caused a large bathochromic shift of 67 nm, which had λ_{em} values of 419 and 485 nm. Additionally, it showed a hypsochromic shift in THF (ϵ=7.58) since its λ_{em} decreased to 446 nm. In changing to methanol (ϵ=32.6) a slight bathochromic shift was observed at λ_{em}=463 nm. In acetonitrile (ϵ=37.5) again a hypsochromic shift was detected (λ_{em}=443 nm). Our attempts to measure the light emission in their neat solid states were unsuccessful presumably due to self-quenching phenomenon. However, we measured their light emissions in a polystyrene matrix (Fig. 6), which eliminated the self-quenching,[15] and the results of their optical properties are compiled in Table 2.

Quantum yields are important factors for light-emitting compounds[1] and therefore, understanding how to correlate them with isomeric compounds is of significant interest in the field of materials chemistry. Considering the monosubstituted amines **1b**–**3b**, their quantum yields vary dramatically as shown in Table 2. Compound **1b**, which contained an amino group at the Z position that was directly connected to the quinoline moiety of the molecule, showed a high quantum yield of 45%. Compounds **2b** and **3b**, which contained amino groups attached on to the phenyl ring *para*-(R_6) and *meta*-(R_5) with respect of the quinoline moiety, had very low quantum yields of 9% and 2%, respectively. These results conveyed

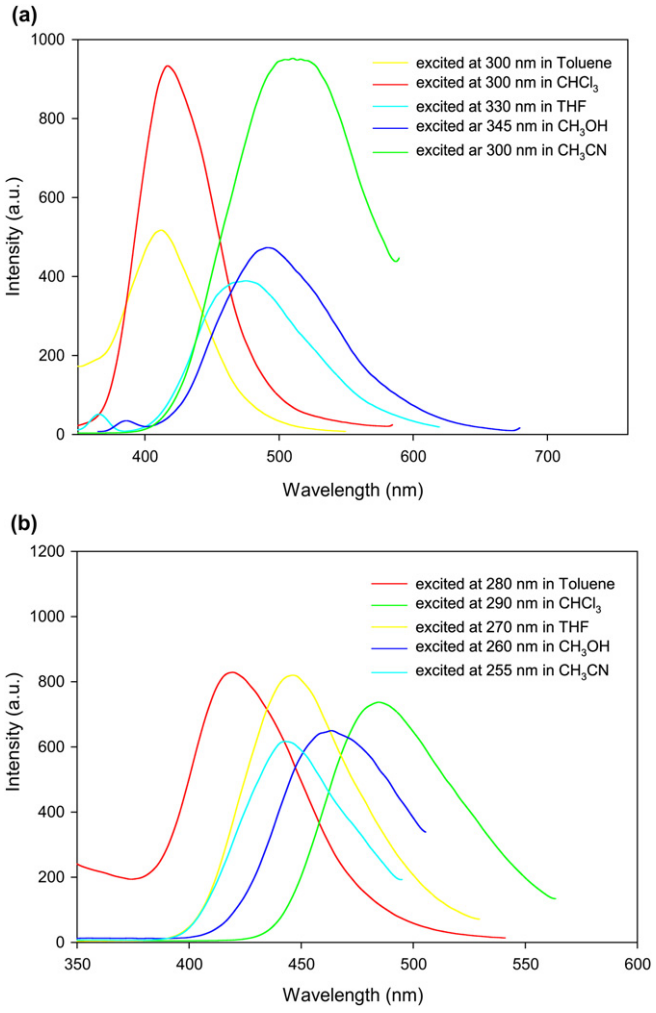


Fig. 5. Photoluminescence spectra of compounds (a) **3b** and (b) **1b** measured in various organic solvents.

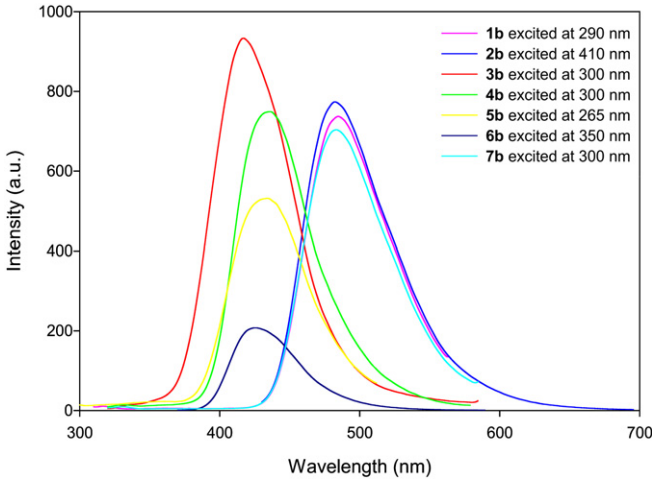


Fig. 4. Photoluminescence spectra of compounds **1b**–**7b** measured in $CHCl_3$.

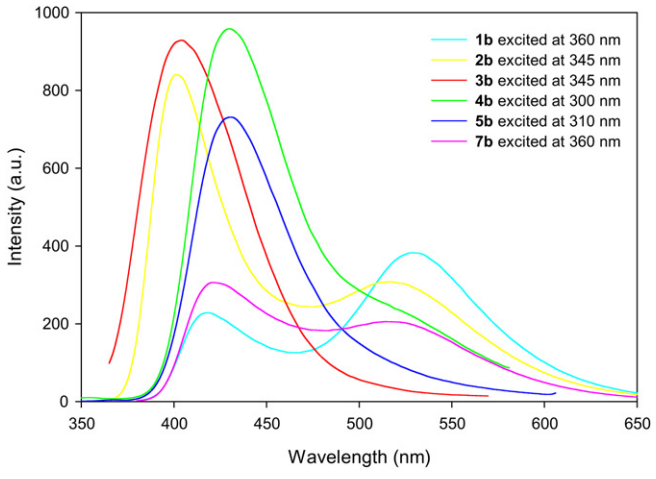


Fig. 6. Photoluminescence spectra of compounds **1b**–**5b** and **7b** measured in polystyrene matrix film cast from $CHCl_3$.

the concept that having an amino group at the Z position is crucial for obtaining a high quantum yield for these compounds. This phenomenon is usually observed in aromatic amines, which are dipolar both in the ground state S_0, and in the excited state S_1. This behavior is in consistent with our results. The common light-emitting aromatic amines include aniline, *N*,*N*-dimethylaniline, 4-aminodiphenyl ether, and aminofluorene.[16] The excellent quantum yields of **4b**–**7b** with the exception of compound **6b** further confirmed these optical properties. The reason for the low quantum yield of **6b** was presumably related to the second amino group *ortho* to the quinoline moiety. This amino group was hydrogen bonded to the nitrogen of the quinoline moiety that was determined from the analysis of its ^{1}H NMR spectrum. The chemical shift of hydrogen bonded aromatic amine protons with quinoline appears further downfield with respect to that of aromatic amine protons signal. This non-covalent interaction results in destabilization of the excited state of the chromophore, which in return lowers the quantum efficiency.

3. Conclusions

In conclusion, we successfully synthesized several quinoline amine compounds by Friedländer condensation reactions and also examined extensively their thermal and optical properties. All compounds formed stable amorphous phases after the first melting transitions of solvent-recrystallized samples as determined with DSC and XRD techniques. Thus, we were able to simplify the procedures to form stable glasses from organic amines, which did not require the utilization of any special techniques including vapor deposition.[5] They emitted blue to green light as well as exhibited solvatochromism phenomenon. Their quantum yields were also suitable for a variety of applications. Additionally, we successfully were able to draw thin smooth fibers from the melts of these quinoline amines and to examine their morphologies with POM and SEM. The understanding for the mechanism of self-assembly of these diamines could lead to the development of new materials in the field of nanotechnology. Overall, their properties were tunable implying their versatility as amorphous molecular materials for various electronic and optoelectronic devices. Moreover, quinoline diamine compounds **4b**–**6b** could be used as asymmetric monomers for the preparation of high performance polymers. Additionally, polymers such as polyamides and polyimides are suitable as charge-transporting layers in optoelectronic devices.[17] We are currently investigating their potential as suitable monomers in the development of poly(pyridinium salt)s,[18] the results of which will be reported elsewhere in due course.

4. Experimental section

4.1. Chemicals and characterization

The ^{1}H and ^{13}C NMR spectra were recorded with an NMR spectrometer equipped with three RF channels operating and 400 MHz and 100 MHz, respectively. Solutions were prepared by dissolving ca. 25 mg of compounds per mL of DMSO-d_6 or $CDCl_3$ with TMS as internal standard. The phase transitions of these compounds were measured using differential scanning calorimetry (DSC) under a nitrogen flow at heating and cooling rates of 10 °C/min. The temperature axis of the DSC thermogram was calibrated with reference standards of high purity indium and tin before use. Compounds of 8–10 mg were used for these analyses. The UV–vis absorption spectra of compounds in various organic solvents were recorded using a UV–visible spectrophotometer in quartz cuvette. Their photoluminescence properties, in both solution and film states, were analyzed using a luminescence spectrophotometer. Quantum yields were analyzed by adjusting the solution absorption using the UV–vis to ca. 0.05 at 350 nm wavelength, the output was measured using the luminescence spectrophotometer at the same wavelength and compared it to known 9,10-diphenylanthracene standard using Eq. 1:

$$\phi_{unk} = \phi_{std}\left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \quad (1)$$

Φ is the fluorescence quantum yield, I is the absorption of the excitation wavelength, A is the area under the emission curve, and η is the refractive index of the solvents used. Subscript std denotes the standard and subscript unk denotes the unknown.[19] The X-ray diffraction studies were performed on finely powdered samples at rt with X-ray diffraction spectrometer using Cu Kα radiation as an X-ray source at 45 kV and 40 mA. The images of hand-drawn fibers with a pair of tweezers from the melts were taken with a polarized optical microscope (POM) equipped with crossed polarizers and a red quarter plate, and a scanning electron microscope (SEM). The calculation of molecular length along the long axis of molecule was obtained using the program of ChemDraw combining energy minimized MM2 calculations.

4.2. Synthetic procedures

Compounds **1a**, **4**–**7a** were successfully prepared by Friedländer condensation reaction as described in the literature.[20a] Synthesis of compound **4a** was reported with a yield of 55% and mp of 276–277 °C.[20a] In another report, **4a** was also synthesized by using diphenyl phosphate, but neither yield nor melting point was repoted.[20b] In our hands, we were able to prepare it with a yield as high as 87% and mp of 281 °C as examined with the DSC measurement. Furthermore, the structure of **4a** was not confirmed in the literature by any means.[20a,b] We determined its structure by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. Compounds **2a** and **3a** were prepared by employing different procedure since 2-aminobenzophenone was unreactive in the identical synthetic reaction conditions.[20b,c] All amino compounds **1b**–**7b** were successfully prepared via hygrogenation with hydrazine monohydrate over Pd/C catalyst in ethanolic solutions in good yields. Compound **4b** has been reported in literature in poor yield of 57% and mp of 191–192 °C.[20b] We were able to make it in 81% yield and mp 194 °C. Note here that compound **2b** was prepared in one-step synthesis via microwave chemistry in good yield of 80%.[20d]

*4.2.1. 6-Nitro-2,4-diphenyl-quinoline (**1a**).* A total of 7.50 g (31.0 mmol) 2-amino-5-nitrobenzophenone and 3.75 g (31.0 mmol) acetophenone was added to 60.0 mL of acetic acid. Sulfuric acid (6 mL) was added to the reaction mixture, which was heated to reflux for 4 h. After completion, the reaction was cooled down to rt. It was poured slowly into ammonium hydroxide/ice mixture (150/120 by volume in mL). The precipitate was collected and washed with hot water and ethanol sequentially. The crude compound was recrystallized from DMF to afford 9.40 g (28.8 mmol, yield 93%) of a spongy white compound. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 8.68 (d, J=2.53 Hz, 1H), 8.50 (dd, J=9.2, 2.58 Hz, 1H), 8.40 (m, 2H), 8.33 (d, J=9.2 Hz, 1H), 8.27 (s, 1H), 7.73 (m, 2H), 7.71–7.64 (m, 3H), 7.62–7.56 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 159.0, 150.6, 150.2, 144.8, 137.5, 136.2, 131.4, 130.58, 129.6, 129.2, 128.9, 128.9, 127.8, 124.0, 123.1, 122.3, 120.3. [Found: C, 77.19; H, 4.40; N, 8.79. requires $C_{21}H_{14}N_2O_2$ (326.36): C, 77.29; H, 4.32; N, 8.58%].

*4.2.2. 6-Nitro-2(4-nitrophenyl)-4-phenylquinoline (**4a**).* Yield=87%, recrystallized from DMF. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 8.68 (d, J=2.10 Hz, 1H), 8.60 (d, J=8.8 Hz, 2H), 8.48 (dd, J=9.2, 2.32 Hz, 1H), 8.35 (t, J=7.3 Hz, 3H), 8.29 (s, 1H), 7.65 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 157.7, 152.0, 150.9, 149.6, 146.0, 144.36, 136.9, 132.6, 130.6, 130.1, 129.9, 129.4, 125.4, 124.4, 123.8, 123.1,

121.6, 121.4. [Found: C, 67.80; H, 3.60; N, 11.42. requires $C_{21}H_{13}N_3O_4$ (371.36): C, 67.92; H, 3.53; N, 11.32%].

*4.2.3. 6-Nitro-2(3-nitrophenyl)-4-phenylquinoline (**5a**).* Yield=88%, recrystallized from DMF. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.12 (t, J=1.98 Hz, 1H), 8.77 (d, J=8.0 Hz, 1H), 8.68 (d, J=2.5 Hz, 1H), 8.48 (dd, J=9.2, 2.54 Hz, 1H), 8.33 (m, 3H), 7.84 (t, J=8.0 Hz, 1H), 7.75–7.57 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 151.8, 149.6, 148.0, 145.7, 142.8, 140.4, 139.5, 131.1, 129.9, 129.8, 129.3, 128.7, 127.7, 122.3, 119.2, 115.0, 112.7, 103.1. [Found: C, 67.76; H, 3.63; N, 11.47. requires $C_{21}H_{13}N_3O_4$ (371.36): C, 67.92; H, 3.53; N, 11.32%].

*4.2.4. 6-Nitro-2(2-nitrophenyl)-4-phenylquinoline (**6a**).* Yield=56%, recrystallized from DMF. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 8.92 (d, J=2.5 Hz, 1H), 8.51 (dd, J=9.2, 2.53 Hz, 1H), 8.28 (d, J=9.2 Hz, 1H), 8.06 (dd, J=8.1, 1.01 Hz, 1H), 7.86–7.73 (m, 2H), 7.61 (m, 7H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 159.0, 151.7, 150.7, 146.2, 136.4, 135.2, 133.2, 132.1, 131.8, 130.4, 129.8, 129.8, 129.4, 125.2, 125.1, 123.6, 123.2, 122.7. [Found: C, 67.75; H, 3.58; N, 11.43. requires $C_{21}H_{13}N_3O_4$ (371.36): C, 67, 92; H, 3.53; N, 11.32%].

*4.2.5. 6-Nitro-2(4-hexylphenyl)-4-phenylquinoline (**7a**).* Yield=92%, recrystallized from methanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 8.60 (d, J=2.5 Hz, 1H), 8.41 (dd, J=9.2, 2.57 Hz, 1H), 8.23 (dd, J=8.7, 6.28 Hz, 3H), 8.15 (s, 1H), 7.76–7.57 (m, 5H), 7.32 (d, J=8.2 Hz, 2H), 2.61 (t, J=7.6 Hz, 2H), 1.57 (m, 2H), 1.27 (d, J=16.3 Hz, 6H), 0.83 (dd, J=9.1, 4.77 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 159.8, 151.2, 151.0, 146.1, 146.1, 137.0, 135.8, 132.1, 130.4, 130.0, 129.8, 129.7, 128.5, 124.7, 123.8, 123.7, 123.0, 121.0, 35.7, 31.8, 31.4, 29.0, 22.8, 14.6. [Found: C, 78.88; H, 6.35; N, 6.99. requires $C_{27}H_{26}N_2O_2$ (410.52): C, 79.00; H, 6.38; N, 6.82%].

*4.2.6. 2(4-Nitrophenyl)-4-phenylquinoline (**2a**).* A total of 4.00 g (20.3 mmol) 2-aminobenzophenone, 3.35 g (20.3 mmol) 4′-nitroacetophenone, and 20.3 g (81.1 mmol) of diphenyl phosphate was heated to 140 °C for 6 h under nitrogen flow. Upon completion of the reaction, the mixture was cooled down to rt and was precipitated in 10% triethylamine/methanol. The crude product was collected and washed with excess methanol. The compound was eluted in chloroform through a column chromatography on silica gel. It was recrystallized from acetonitrile to afford 7.00 g (21.5 mmol, yield 85%) of pale yellow crystals. ^{1}H NMR (400 MHz, TFA-d_1) δ ppm 8.66 (d, J=7.35 Hz, 2H), 8.47 (dd, J=8.44, 5.22 Hz, 2H), 8.35 (d, J=7.36 Hz, 2H), 8.33–8.24 (m, 2H), 8.06 (t, J=7.75 Hz, 1H), 7.77 (m, 5H). ^{13}C NMR (100 MHz, TFA-d_1) δ ppm 162.9, 162.3, 161.9, 161.5, 161.0, 151.3, 150.2, 138.8, 136.6, 136.3, 134.2, 131.3, 130.8, 129.6, 129.1, 128.9, 127.8, 126.9, 124.8, 121.0, 120.1, 118.5, 115.6, 112.8, 110.0. [Found: C, 77.55; H, 4.71; 8.95. requires $C_{21}H_{14}N_2O_2$ (326.36): C, 77.29; H, 4.32; N, 8.58%].

*4.2.7. 2(3-Nitrophenyl)-4-phenylquinoline (**3a**).* Yield=89%, after precipitation in 10% triethylamine/methanol to afford the crude product. It was washed with excess methanol recrystallized from acetonitrile to give light purple crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.07 (t, J=1.9 Hz, 1H), 8.58 (d, J=7.8 Hz, 1H), 8.34–8.28 (m, 1H), 8.26 (d, J=8.4 Hz, 1H), 7.93 (d, J=7.8 Hz, 1H), 7.86 (s, 1H), 7.77 (ddd, J=8.3, 6.9, 1.3 Hz, 1H), 7.69 (dd, J=9.9, 6.02 Hz, 1H), 7.55 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.9, 150.0, 148.8, 141.3, 137.9, 133.3, 130.2, 130.0, 129.9, 129.8, 129.5, 128.7, 127.1, 126.1, 125.8, 123.9, 122.4, 118.6. [Found: C, 77.23; H, 4.43; N, 8.50. requires $C_{21}H_{14}N_2O_2$ (326.36): C, 77.29; H, 4.32; N, 8.58%].

*4.2.8. 6-Amino-2,4-diphenyl-quinoline (**1b**).* An ethanol suspension (50.0 mL) of the 7.50 g (23.0 mmol) 6-amino-2,4-diphenyl-quinoline was heated to 50.0 °C in presence of 0.10 g of Pd/C and 5.00 mL of hydrazine monohydrate were added over 30 min to this suspension. The reaction mixture became clear as the reaction proceeded. It was kept at reflux for another 12 h. Upon completion of the reaction, the mixture was filtered over Celite twice to remove the Pd/C catalyst. The ethanol was removed under reduced pressure. The crude product was recrystallized from isopropanol to afford 6.20 g (20.9 mmol, yield 91%). Note the crystals grew slowly. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 8.20 (m, 2H), 7.85 (d, J=9.0 Hz, 1H), 7.74 (s, 1H), 7.61–7.54 (m, 4H), 7.53–7.43 (m, 3H), 7.43–7.35 (m, 1H), 7.20 (dd, J=9.0, 2.5 Hz, 1H), 6.82 (d, J=2.4 Hz, 1H), 5.67 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 151.0, 148.3, 146.0, 142.9, 139.9, 139.4, 131.3, 130.0, 129.6, 129.5, 129.4, 129.0, 128.7, 127.8, 127.2, 122.5, 119.2, 103.1. [Found: C, 85.01; H, 5.54; N, 9.50. requires $C_{21}H_{16}N_2$ (296.37): C, 85.11; H, 5.44; N, 9.45%].

*4.2.9. 2(4-Aminophenyl)-4-phenylquinoline (**2b**).* Yield=48%, the compound was eluted in chloroform through a column chromatography on silica gel, it was vacuum dried and it was recrystallized from isopropanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 8.06 (dd, J=11.2, 8.5 Hz, 3H), 7.86 (s, 1H), 7.74 (m, 2H), 7.65–7.51 (m, 5H), 7.46 (dd, J=11.2, 4.0 Hz, 1H), 6.70 (d, J=8.6 Hz, 2H), 5.58 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 156.0, 150.5, 148.1, 147.8, 137.8, 129.4, 129.1, 128.5, 128.3, 125.5, 125.4, 125.0, 124.3, 117.6, 113.6. [Found: C, 84.90; H, 5.53; N, 9.64. requires $C_{21}H_{16}N_2$ (296.37): C, 85.11; H, 5.44; N, 9.45%].

*4.2.10. 2(3-Aminophenyl)-4-phenylquinoline (**3b**).* Yield=82%, recrystallized from isopropanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.23 (d, J=8.4 Hz, 1H), 7.78 (s, 1H), 7.75–7.67 (m, 1H), 7.61–7.57 (m, 1H), 6.78 (dd, J=7.8, 1.7 Hz, 1H), 7.29 (t, J=7.8 Hz, 1H), 7.57–7.48 (m, 6H), 7.46 (m, 1H), 7.89 (d, J=7.8 Hz, 1H), 3.79 (d, J=0.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 157.0, 149.0, 148.7, 147.0, 140.7, 138.4, 130.0, 129.7, 129.5, 128.6, 128.3, 126.2, 125.8, 125.6, 119.5, 117.9, 116.2, 114.1. [Found: C, 85.07; H, 5.38; N, 9.30. requires $C_{21}H_{16}N_2$ (296.37): C, 85.11; H, 5.44; N, 9.45%].

*4.2.11. 6-Amino-2(4-aminophenyl)-4-phenylquinoline (**4b**).* Yield=81%, recrystallized from isopropanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 7.92 (d, J=8.6 Hz, 2H), 7.75 (d, J=8.9 Hz, 1H), 7.63–7.57 (m, 1H), 7.57–7.52 (m, 4H), 7.52–7.45 (m, 1H), 7.13 (dd, J=8.9, 2.4 Hz, 1H), 6.77 (d, J=2.4 Hz, 1H), 6.66 (d, J=8.7 Hz, 2H), 5.37 (s, 2H), 5.48 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 151.9, 150.2, 147.3, 145.7, 142.9, 139.7, 130.7, 129.9, 129.3, 128.6, 128.2, 127.4, 127.0, 122.1, 118.3, 114.4, 103.6. [Found: C, 80.86; H, 5.31; N, 13.71. requires $C_{21}H_{17}N_3$ (311.39): C, 81.00; H, 5.50; N, 13.49%].

*4.2.12. 6-Amino-2(3-aminophenyl)-4-phenylquinoline (**5b**).* Yield=88%, recrystallized from ethanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 7.81 (d, J=8.9 Hz, 1H), 7.67–7.44 (m, 7H), 7.31 (d, J=7.8 Hz, 1H), 7.25–7.09 (m, 2H), 6.80 (d, J=2.4 Hz, 1H), 6.62 (dd, J=7.8, 2.2 Hz, 1H), 5.65 (s, 2H), 5.19 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 151.8, 149.6, 148.0, 145.7, 142.8, 140.4, 139.5, 131.1, 129.9, 129.8, 129.3, 128.7, 127.7, 122.3, 119.2, 115.0, 112.7, 103.1. [Found: C, 80.92; H, 5.61; N, 13.77. requires $C_{21}H_{17}N_3$ (311.39): C, 81.00; H, 5.50; N, 13.49%].

*4.2.13. 6-Amino-2(2-aminophenyl)-4-phenylquinoline (**6b**).* Yield=62%, the compound was eluted in chloroform in a silica gel column chromatography for purification. It was then recrystallized from isopropanol/ether (98/2 by volume in mL). Note that it is difficult to get the correct ratio of this solvent-pair mixture because of the volatility of ether. Crystals grew very slowly (2–3 days). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 7.78 (d, J=8.9 Hz, 1H), 7.73–7.65 (m, 1H), 7.59 (s, 1H), 7.52 (m, 5H), 7.17 (dd, J=8.9, 2.4 Hz, 1H), 7.13–7.03 (m, 1H), 6.92 (s, 2H), 6.66–6.56 (m, 1H), 5.61 (s, 2H), 6.80 (t, J=5.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 153.9, 148.7, 148.1, 146.0, 141.2, 139.4, 130.4, 129.9, 129.7, 129.3, 128.7, 126.7, 122.2,

120.9, 120.7, 117.1, 116.4, 103.4. [Found: C, 80.99; H, 5.62; N, 13.53. requires $C_{21}H_{17}N_3$ (311.39): C, 81.00; H, 5.50; N, 13.49%].

*4.2.14. 6-Amino-2(4-hexylphenyl)-4-phenylquinoline (**7b**).* Yield=76%, recrystallized from isopropanol/water. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 8.09 (d, J=8.3 Hz, 2H), 7.81 (d, J=8.9 Hz, 1H), 7.70 (s, 1H), 7.62–7.52 (m, 4H), 7.52–7.47 (m, 1H), 7.27 (d, J=8.3 Hz, 2H), 7.17 (dd, J=8.9, 2.46 Hz, 1H), 6.79 (d, J=2.4 Hz, 1H), 5.61 (d, J=7.0 Hz, 2H), 2.48 (td, J=3.7, 1.8 Hz, 2H), 1.57 (dd, J=14.0, 7.0 Hz, 2H), 1.36–1.15 (m, 6H), 0.84 (t, J=14.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 151.1, 148.1, 145.9, 143.5, 142.9, 139.4, 137.4, 131.1, 130.0, 129.3, 128.7, 127.7, 127.1, 122.4, 119.0, 103.7, 35.6, 31.8, 31.5, 29.0, 22.8. [Found: C, 85.30; H, 7.55; N, 7.56, requires $C_{27}H_{28}N_2$ (380.54): C, 85.22; H, 7.42; N, 7.36%].

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Supplementary data

Structures and designations, and ^{1}H and ^{13}C NMR spectra of all compounds are provided. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2010.09.108. These data include MOL files and InChIKeys of the most important compounds described in this article.

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