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Tetrahedron Letters 48 (2007) 5383–5387

Tetrahedron
Letters

Synthesis, optical, and thermal properties of conjugated, bispyridyl and tetrapyridyl compounds by Knoevenagel reaction

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Received 28 May 2007; revised 5 June 2007; accepted 5 June 2007
Available online 9 June 2007

Abstract—A series of conjugated, bispyridyl and tetrapyridyl compounds were synthesized from either terephthalaldehyde or isophthalaldehyde and activated pyridyl compounds by Knoevenagel reaction on heating in acetic anhydride in presence of acetic acid and their optical and thermal properties were examined. All of them exhibited photoluminescence in chloroform, tetrahydrofuran, and dimethyl sulfoxide as well as in solid state. In solid state, their emission spectra exhibited bathochromic shifts when compared with those in less or more polar solvents. Some compounds emitted UV light both in polar solvents and in the solid state; other compounds emitted UV light in polar solvents, but emitted visible light in the solid state.
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The Knoevenagel reaction, when applied to activated methyl derivatives of pyridine or other nitrogen heterocycles, directly leads to arylene–vinylene–heteroarylene structures, which constitute the basic structural elements of entirely π-conjugated molecules. They are essentially an interesting class of organic molecules, which have many applications in the field of supramolecular chemistry via hydrogen-bonding and in optoelectronic devices.[1–5]

Although other organic reactions like Heck and Wittig reactions yield similar structures, but the Knoevenagel reaction has the advantage of being a simple and easy reaction to perform, since water is the only other product. There are no unstable reactive intermediates involved or other special chemical reagents necessary for this reaction yielding the desired reaction products, all of these elements make this reaction environmentally friendly. Furthermore, the reaction products of this reaction are usually *trans*-alkenes, since it is a thermal condensation reaction and occurs at relatively high temperature. In contrast, Wittig reaction produces a mixture of *cis*/*trans*-alkenes. This Knoevenagel reaction can be usually catalyzed with either organometallic or base or acid catalysts.

In this Letter, we report a facile synthetic approach to a series of conjugated, bispyridyl and tetrapyridyl compounds, **1**–**5**, via Knoevenagel reaction (Scheme 1), which was carried in acetic anhydride in the presence of acetic acid.[6] Their chemical structures were characterized by ^{1}H ^{13}C NMR spectra and elemental analyses. Their optical and thermal properties were studied with the aim of understanding the structure–physical property relationships and developing novel organic materials.

We synthesized compound **1** in moderate yield (57%) by Knoevenagel reaction.[6] It was previously synthesized from γ-picoline and terephthalaldehyde on heating by using $ZnCl_2$ as a catalyst in a sealed tube at 210–215 °C for 50 h in 60% yield (mp 262–263 °C).[7] It was also prepared by the reaction of 2 equiv of deprotonated γ-picoline, prepared by the addition of appropriate amount of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at low temperature, with terephthalaldehyde, followed by dehydration of the intermediate dialcohol with $POCl_3$ in anhydrous pyridine with a yield of 60%.[8] Lu et al.[4] reported the mp of **1** as 265 °C as determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. Unfortunately, no detailed synthetic procedure for this compound was available. Recently, Lin et al.[5] reported the synthesis of **1**

Keywords: Conjugated bispyridyls; Photoluminescence; Differential scanning calorimetry.

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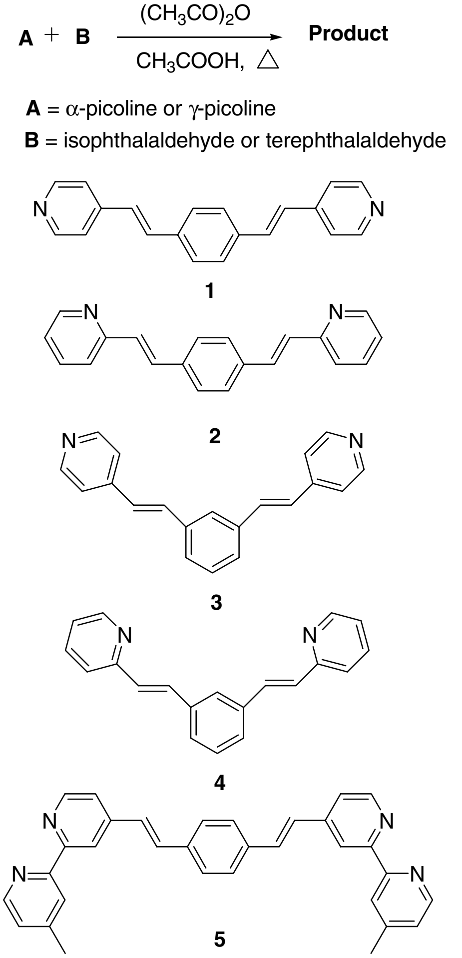
doi:10.1016/j.tetlet.2007.06.019



Scheme 1. Compounds **1**–**5** synthesized via Knoevenagel reaction.

from *p*-xylene in three steps: *N*-bromosuccinimide (NBS) bromination, formation of phosphonium salt and Wittig reaction with γ-picoline. The yield of NBS bromination product was not given, since it was used for the subsequent step without any purification. However, compound **1** was purified by column chromatography over silica gel (eluent: ethyl acetate/hexane = 5:1). The yields for the second and third steps were 46% and 16%, respectively. Thus, the yield and purity of this compound via Knoevenagel reaction were far superior to the methods described in the literature,[4,5,7,8] since this reaction is simple to carry out in a single-step without any special reagents or anhydrous solvents or any uncommon pieces of glassware.

Similarly, compound **2** was also prepared by Knoevenagel reaction and it was found that the yield was low (28%) for 24 h reaction time when compared with the yield of **1**. However, when the reaction was carried out for a long reaction time of 48 h, the yield increased to 46%. No attempts were made for the optimization of the conditions for this reaction. Since the Witting reaction produced low yield (56%) of **2**,[7] Hasegawa et al.[9] reported a method wherein this compound was prepared via Knoevenagel reaction by heating to reflux a mixture of terephthalaldehyde (1.0 equiv) and α-picoline (2.0 equiv) in benzoic anhydride for 8 h with a yield of 75%. Recently, Lin et al.[5] also reported the synthesis of **2** from *p*-xylene in three steps: *N*-bromosuccinimide (NBS) bromination, formation of phosphonium salt and Wittig reaction with α-picoline. The yield of NBS bromination product was not given, since it was used for the subsequent step without purification. However, the compound **2** was also purified by column chromatography on silica gel (eluent: ethyl acetate/hexane = 5:1). The yields for the second and third steps were 46% and 17%, respectively. In this regard, our method was slightly inferior to that of Hasegawa et al.[9] with regard to yield but superior to that of Lin et al. (single-step vs sequential three-step).[5]

Compounds **3** and **4** were prepared via Knoevenagel condensation reaction of γ-picoline and α-picoline with isophthalaldehyde under identical conditions with those of compounds **1** and **2** with yields of 28% and 39%, respectively.[6] The compound **5** was also prepared in a single step procedure by using this reaction with a poor yield of 6%. It was previously prepared in two steps from the reaction of 1 equiv of deprotonated 4,4′-dimethyl 2,2′-bipyridine, which was again prepared by the addition of 1 equiv of LDA in THF at low temperature, with 0.5 equiv terephthalaldehyde, followed by dehydration of the intermediate dialcohol with $POCl_3$ in anhydrous pyridine. Unfortunately, no information regarding the overall yield for the synthesis of **5** is available.[10]

Since all of the compounds, **1**–**5**, contained chromophores, they were examined for their optical properties by UV–vis absorption and photoluminescence spectra. The optical properties of compounds **1** and **2** both in dimethyl sulfoxide (DMSO) solutions and in the solid state including their photoreactivity have been studied extensively by Ebied et al.[11–14] and others.[5] In $CHCl_3$ solution of compound **1** at 6.80×10^{-8} M showed a major λ_{em} at 401 along with a shoulder peak at 383 nm when excited at 343 nm. Similarly, it exhibited λ_{em} at 398 along with a shoulder peak at 381 nm at identical concentration in THF, when excited at 345 nm. As expected, in highly polar solvent like DMSO at identical concentration both the λ_{em} peak (408 nm) and shoulder peak (390 nm), when excited at 345 nm, were slightly shifted bathochromically because of the more polar excited state than the ground state. In the solid state, it exhibited λ_{em} at 433 nm when excited at 250 nm. At other excitation wavelengths, it showed not only a major λ_{em} peak at ca. 433 nm but also a shoulder peak in the range of 544–549 nm. This shoulder peak is related to the excimer emission that originates from the excited state molecular aggregation in the solid state.

Compound **2** at 6.86×10^{-8} M in $CHCl_3$ solution showed two λ_{em} peaks at 386 and 405 nm when excited at 345 nm. Similarly, it exhibited λ_{em} peaks at 382 and 402 nm at identical concentration in THF. As expected, in highly polar solvent like DMSO at identical concentration both the λ_{em} peaks (388 and 407 nm) were slightly shifted bathochromically because of the more polar excited state than the ground state. In the solid state, it exhibited λ_{em} peaks at 435 and 461 nm when excited at 250 nm. At other excitation wavelengths, it also showed two λ_{em} peaks at ca. 435 nm and 461 nm. Thus, the λ_{em} peaks of this compound were independent on the excitation wavelengths used. The bathochromic shifts of these λ_{em} peaks in the solid state when compared with those of solutions are related to its molecular aggregation because of the π–π stacking effect. For compounds **1** and **2** both the λ_{max} peaks of UV–vis absorption spectra in various solvents and λ_{em} peaks are highly dependent on the concentrations, since these compounds undergoes aggregation even in dilute solutions.[5,10–14] Furthermore, these compounds emitted UV light in various solutions, but emitted blue light in the solid state.

The λ_{max} values of **3** in UV–vis absorption spectra in $CHCl_3$ ($\varepsilon = 5.0$), THF ($\varepsilon = 7.6$), and DMSO ($\varepsilon = 48.9$) were 305, 305, and 310 nm, respectively. As expected, in more polar solvent DMSO, its λ_{max} was shifted to longer wavelength by 5 nm suggestive of its $\pi \rightarrow \pi^*$ transition. Figure 1 shows the photoluminescence spectra of **3** recorded in various solvents as well as in the solid state. In less polar solvents like $CHCl_3$ and THF, it had λ_{em} peaks at 373 and 374 nm, respectively, when excited at 295 nm. At an identical excitation wavelength and at identical concentration in DMSO, it exhibited λ_{em} at 381 nm, which is bathochromically shifted by 7 or 8 nm when compared with those in less polar solvents. The observed bathochromic shifts with the increase in solvent polarities indicated that the excited state of this molecule was more polar than the ground state. However, in the solid state, its λ_{em} peak was located at 386 nm when excited at 230 nm, which was further bathochromically shifted when compared with those in both less and more polar solvents. At other higher excitation wavelengths, its emission wavelength was shifted slightly bathochromically. The excitation spectra obtained in various solvents, when monitored at 378, 375, and 380 nm, showed at λ_{ex} at ca. 298 nm. In the solid state, there were three λ_{ex} peaks at 215, 232, and 334 nm when monitored at 390 nm (not shown). Its photoluminescence λ_{em} peaks both in solutions and in the solid state were blue shifted when compared with those of compounds **1** and **2**, since it contained *m*-phenylene moiety instead of *p*-phenylene present in the latter compounds. Thus, it emitted UV light both in polar solvents and in the solid state.

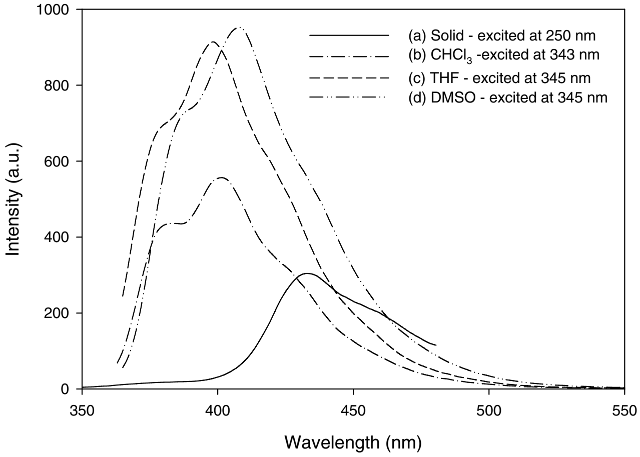


Figure 1. Photoluminescence spectra of compound **3** measured in (a) solid state, (b) $CHCl_3$, (c) THF, and (d) DMSO.

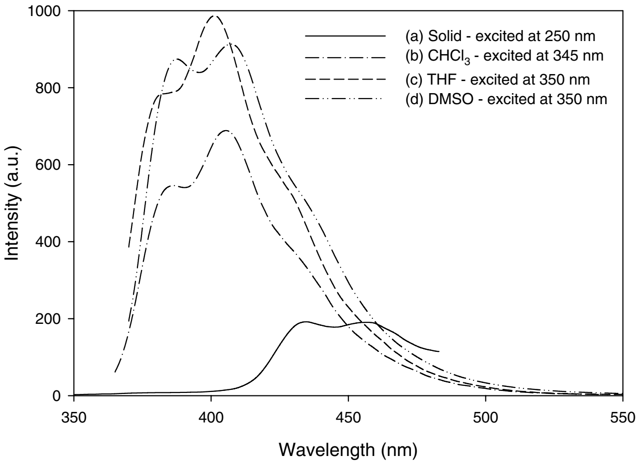


Figure 2. Photoluminescence spectra of compound **4** measured in (a) solid state, (b) $CHCl_3$, (c) THF, and (d) DMSO.

The two λ_{max} values of **4** in UV–vis absorption spectra were 280 and 315 in $CHCl_3$ ($\varepsilon = 5.0$), 280 and 315 in THF ($\varepsilon = 7.6$), and 285 and 320 nm in DMSO ($\varepsilon = 48.9$), respectively. As expected, in more polar solvent DMSO, its λ_{max} peaks were shifted to longer wavelengths by 5 nm suggestive of its $\pi \rightarrow \pi^*$ transition. Figure 2 shows the photoluminescence spectra of this compound recorded in various solvents as well as in the solid state. In $CHCl_3$ it showed two λ_{em} peaks at 364 and 375 nm when excited at 310 nm. In THF, it had two λ_{em} peaks at 361 and 375 nm when excited at 308 nm. At an almost identical excitation wavelength and at identical concentration in DMSO, it exhibited λ_{em} peak at 379 nm along with an indistinct shoulder peak, which is bathochromically shifted by 4 or 5 nm when compared with those in less polar solvents. The observed bathochromic shifts with the increased solvent polarities indicated that the excited state of this molecule was more polar than the ground state. However, in the solid state, its λ_{em} peak was located at 382 nm when excited at 230 nm, which was further bathochromically shifted when compared with those in both less and more polar solvents. At other higher excitation wavelengths, its emission wavelength was shifted slightly bathochromically. The excitation spectra obtained in various solvents, when monitored at 375, 375, and 380 nm, showed λ_{ex} at ca. 308 nm. In the solid state, there were three λ_{ex} peaks at 213, 231, and 350 nm when monitored at 380 nm (not shown). Like those of photoluminescence spectra of compound **3**, its photoluminescence λ_{em} peaks both in solutions and in the solid state were blue shifted when compared with those of **1** and **2**, since it contained *m*-phenylene moiety instead of *p*-phenylene present in latter compounds. Similar to the compound **3**, it also emitted UV light both in polar solvents and in the solid state.

Compound **5** in $CHCl_3$ solution showed two λ_{em} peaks at 387 and 409 nm, when excited at 345 nm. In THF

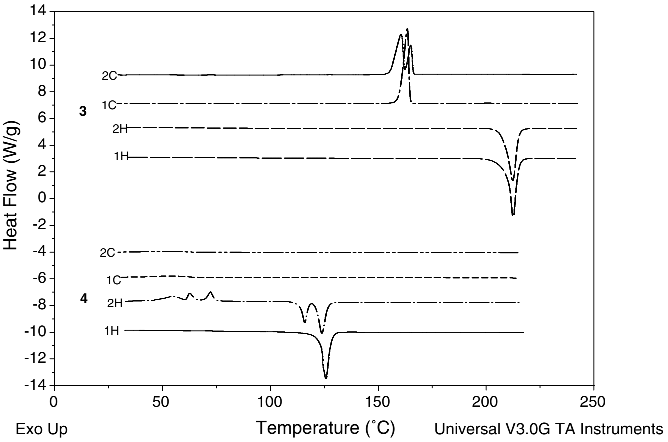


Figure 3. DSC thermograms of compounds **3** and **4** obtained at heating and cooling rates of 10 °C/min.

solution, it also exhibited two λ_{em} peaks at 385 and 405 nm, when excited at 350 nm. In the highest polar solvent DMSO, its two λ_{em} peaks were shifted bathochromically to 397 and 413 nm, when excited at 345 nm. Its λ_{em} peak in the solid state was also shifted bathochromically to 471 nm, when excited at 412 nm, because of the aggregation in solid state and because of the π–π stacking effect. It showed the highest bathochromic shift when compared with other compounds **1**–**4** in the solid state, since its structure contained two additional conjugated 4-methyl pyridyl rings linked via the *ortho*-position. In the solid state, its excitation spectrum consisted of a number of λ_{ex} peaks that ranged from 212 to 420 nm when monitored at 470 nm. In contrast, it showed only two λ_{ex} peaks at 269 and 352 nm in $CHCl_3$, when monitored at 385 nm. Similarly, it also showed two λ_{ex} peaks at 271 and 354 nm in DMSO, when monitored at 414 nm. It emitted UV light in polar solvents, but emitted visible light in the solid state.

The thermal properties of compounds **1**–**5** including the monoaldehyde were studied by thermogravimetric analysis (TGA) and DSC. The TGA results revealed that all of the compounds had excellent thermal stability in the temperature range of 218–341 °C, the temperature at which the loss of 5 wt % of each of these compounds occurred at a heating rate of 10 °C/min in nitrogen. Compound **1** exhibited an onset temperature of melting (T_m) at 273 °C with enthalpy change (ΔH) of 8.7 kcal/mol and peak maximum at 275 °C in the first heating cycle. In the first cooling cycle, there was a crystallization exotherm (T_c) at 243 °C with $\Delta H = 7.4$ kcal/mol. Compound **2** showed a T_m at 233 °C with $\Delta H = 9.4$ kcal/mol and a T_c at 192 °C with $\Delta H = 5.4$ kcal/mol in the first heating and cooling cycles, respectively. Figure 3 shows the DSC thermograms of compounds **3** and **4** obtained at heating and cooling rates of 10 °C/min. Compound **3** recrystallized from $CHCl_3$/acetone showed a T_m at 210 °C with $\Delta H = 7.8$ kcal/mol and a T_c at 164 °C with $\Delta H = 6.9$ kcal/mol in the first heating and cooling cycles, respectively. In the second heating cycle, its melting endotherm shifted slightly to lower temperature with slightly reduced ΔH. However, there were two exotherms in the second cooling cycle of its DSC thermogram. Compound **4** recrystallized from methanol/water showed a T_m at 124 °C with $\Delta H = 5.8$ kcal/mol in the first heating cycle. However, it showed an indistinct, broad crystallization exotherm in the first cooling cycle suggesting that it had great difficulty in crystallization in the cooling cycle. However, in the subsequent second heating cycle, it showed three cold crystallization exotherms followed by two melting endotherms at 114 ($\Delta H = 1.7$ kcal/mol and 121 °C ($\Delta H = 3.3$ kcal/mol), respectively. In the second cooling cycle, as was similar to the first cooling cycle, there was an indistinct, broad crystallization exotherm (Fig. 3) because of a very slow crystallization. Compound **5** exhibited two endotherms at 142 ($\Delta H = 0.5$) and 233 °C ($\Delta H = 7.9$ kcal/mol), respectively, in the first heating cycle. In the first cooling cycle, there was T_c at 223 °C ($\Delta H = 7.4$ kcal/mol). In the second heating and cooling cycles, there were a T_m at 229 and a T_c at 219 °C, respectively, both at slightly reduced ΔH. The low temperature endotherm in the first heating cycle was presumably related to the crystal–crystal transition.

In conclusion, we have presented facile synthetic procedures for the preparation of a series of bispyridyl and tetrapyridyl compounds by Knoevenagel reaction. Their optical properties and thermal properties were examined. Some of them emitted UV light both in polar solvents and in the solid state, other compounds emitted UV light in polar solvents, but emitted visible light, at least, in the solid state. They had excellent thermal stability in the temperature range of 218–341 °C in nitrogen. These compounds could be promising materials in optical devices including their use in laser dyes technology.

Acknowledgments

P.K.B. acknowledges the University of Nevada Las Vegas for start-up, Stimulation, Implementation, Transition and Enhancement (SITE), New Investigation Award (NIA), and Planning Initiative Award (PIA) grants, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and an award from Research Corporation for the support of this research.

Supplementary data

The ^{1}H and ^{13}NMR spectra of **1**, **2**, and **5** (Figs. S1–S3), their photoluminescence spectra in solid state, $CHCl_3$, THF, and DMSO (Figs. S4–S6), and DSC thermograms of a monoaldehyde (Fig. S7) are provided as supplementary data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.019.

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6. *General procedure for Knoevenagel condensation reaction for compound* **1**: 3.4 g (25.3 mmol) of terephthalaldehyde and 4.8 g (53.2 mmol) of γ-picoline was heated to reflux for 24 h in 3 mL of acetic acid and 5 mL of acetic anhydride at 135 °C. The reaction mixture was cooled down to rt. It was placed in 100 mL of aqueous 6 M HCl. The resulting precipitate was collected and subsequently washed repeatedly with copious water. The filtrate was neutralized with 3 M NaOH. Upon air-drying, crude product **1** of 5.4 g was collected and then recrystallized from $CHCl_3$/acetone to yield 4.1 g (57%) of orange powder. Anal. Calcd (found) for $C_{20}H_{16}N_2$ (284.36): C, 84.48 (84.09); H, 5.67 (6.02); N, 9.85 (9.96).

   The reaction for compound **2** was set up using similar procedure (24 h) and on an identical scale for compound **1**. After completion of the reaction period, the reaction mixture was cooled down to rt. It was placed in 100 mL of aqueous 6 M HCl. The solution was neutralized with the slow addition of aqueous 3 M NaOH resulting in a precipitate that was washed with a large volume of water. Upon air-drying, 5.7 g of crude product **2** was collected and then recrystallized from $CHCl_3$/acetone to yield 2.0 g (28%) of golden-yellow crystals. Anal. Calcd (found) for $C_{20}H_{16}N_2$ (284.36): C, 84.48 (83.85); H, 5.67 (5.88); N, 9.85 (9.78). The collected mother liquor from recrystallization flask was run through a column chromatography over silica gel. Upon evaporation of solvents, 2.8 g (58%) of bright yellow powder was collected, characterized and identified to be 2-(4-formylstyryl)pyridine-a monoaldehyde byproduct. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.01 (s, 1H), 8.64 (d, $J = 7.2$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.60–7.71 (m, 2H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 16.4$ Hz, 1H), 7.20–7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.83, 154.92, 149.98, 142.86, 137.04, 136.05, 131.63, 131.20, 130.44, 127.76, 123.06, 123.02; Anal. Calcd (found) for $C_{14}H_{11}NO$ (209.25): C, 80.36 (79.99); H, 5.30 (5.70); N, 6.69 (6.98). It had a T_m at 83 °C ($\Delta H = 4.2$ kcal/mol) in the first heating cycle; and its DSC thermograms are shown in Figure S7 in the supplementary material. The reaction for the synthesis of compound **2** was repeated once for a long period of 48 h. Its yield improved significantly giving 3.3 g (46%) of the desired product at the expense of monoaldehyde.

   The procedure for the synthesis of compound **3** was followed identically (24 h) to that for compound **2** up to the neutralization step. After air-drying, it was purified by column chromatography over silica gel eluting in $CHCl_3$. On evaporation of $CHCl_3$ yielded compound **3**, which was then recrystallized from $CHCl_3$/acetone to produce 2.0 g (28%) of light yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.60 (d, $J = 6.4$ Hz, 4H), 7.44 (s, 1H), 7.40 (d, $J = 6.0$ Hz, 4H), 7.26–7.70 (m, 3H), 7.32 (d, $J = 16.4$ Hz, 2H), 7.06 (d, $J = 16.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 150.29, 144.78, 136.96, 133.01, 129.59, 127.47, 126.88, 125.92, 121.14; Anal. Calcd (found) for $C_{20}H_{16}N_2$ (284.36): C, 84.48 (84.09); H, 5.67 (6.03); N, 9.85 (9.97).

   The reaction setup for compound **4** was identical to the described procedure (vide supra). The reaction was carried out for a period of 48 h. Upon cooling, the reaction mixture was treated with 100 mL of 6 M aqueous HCl. When the solution was neutralized with 3 M aqueous NaOH a sticky material was formed. It was allowed to settle down and the solution was decanted. It was washed with fresh distilled water. The material was dried in a vacuum oven. It was eluted in $CHCl_3$ through a column chromatography on silica gel. The solvent was evaporated. The resulting material was lighter in color but still had a sticky appearance. After drying it was dissolved in methanol and was treated with aqueous $NaHSO_3$ to remove any residual aldehydes. Subsequently, the compound was recrystallized for methanol/water mixture to yield 2.8 g (39%) of off-white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.62 (d, $J = 7.6$ Hz, 2H), 7.66–7.80 (m, 4H), 7.43 (s, 1H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.26–7.70 (m, 3H), 7.21 (d, $J = 16$ Hz, 2H), 7.15–7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.64, 149.80, 137.29, 136.92, 132.76, 129.35, 128.46, 127.30, 126.00, 122.47, 122.41; Anal. Calcd (found) for $C_{20}H_{16}N_2$ (284.36): C, 84.48 (84.45); H, 5.67 (6.00); N, 9.85 (10.02).

   The procedure for compound **5** was followed in an identical manner (24 h) to that for compound **2** up to the neutralization step. After air-drying, the crude product was recrystallized from toluene twice resulting 1.5 g of the desired compound, which was eluted in CH_2Cl_2 through a column chromatography on silica gel. The solvent was evaporated to yield 0.4 g (6%) of bright yellow powder. Anal. Calcd (found) for $C_{32}H_{26}N_4$ (466.59): C, 82.38 (81.99); H, 5.62 (6.01); N, 12.01 (12.17).
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