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Reaction of Pyridine with Phenylcyanoacetylene: A New Route to Functionalized Polyconjugated 1,4-Dihydropyridine Systems

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Pyridine reacts with phenylcyanoacetylene under mild conditions (20–25 °C, no catalyst) to unexpectedly give the 2:3 adduct – a *C,N*-functionalized polyconjugated 1,4-dihydropyridine system – containing two 1,4-dihydropyridine cycles and four vinylene units formed by three molecules of phenylcyanoacetylene (the yield is up to 46 %). Other products are higher oligomers of phenylcyanoacetylene terminated by 1,4-dihydropyridine cycles (approx. 30 % yield). Assembly of the 2:3 adduct proceeds regio- and stereoselectively – only one of the possible isomers is formed. The oligomers show paramagnetic and electroconductive properties.

Introduction

Despite the large number of methodologies known for the construction and modification of 1,4-dihydropyridine systems,[1] efforts in this field continue[1–8] due to the importance of these heterocycles in organic synthesis, medicinal chemistry, and biochemistry. 1,4-Dihydropyridines are calcium-channel blockers and NO-releasing agents from endothelium,[5] and some of them exhibit cardiovascular, vasodilator, bronchiodilator, antiatherosclerotic, antitumor, hepatoprotective, antidiabetic, antituberculosis, and anti-ischemic effects.[1] Among the 1,4-dihydropyridines there are also drug-resistance modifiers,[4] antioxidants,[6] and a drug for the treatment of urinary urge incontinence.[7] Interest in 1,4-dihydropyridines is also sustained by their structural closeness to nicotinamide dinucleotide, a cofactor used by many reductases in metabolism.[1,4,5]

Therefore, any progress in the synthesis of 1,4-dihydropyridine systems would contribute to the above areas.

Results and Discussion

Recently, we have found[9,10] that pyridines readily annelate with α-hydroxycyanoacetylenes (20–25 °C, no catalyst, no solvent) to afford cyanomethylene-1,3-oxazolidino[3,2-*a*]-1,2-dihydropyridines. Further investigations into the synthetic potential of zwitterionic adducts of pyridines with cyanoacetylenes aimed at the design of functionalized dihydropyridine assemblies led us to check the reaction of pyridine with phenylcyanoacetylene (**1**). Our experiments showed that the reaction proceeds smoothly (room temperature, no catalyst) and gives surprising results, which are briefly discussed in this paper. Instead of the expected 1:1 and 2:1 adducts, i.e. condensed dihydropyridines **2** and **3**, we isolated (in a yield around 50%) the 2:3 adduct (two molecules of pyridine and three molecules of **1**) (*Z*)-3-{4-[1-cyano-2-{1-[(*Z*)-3-nitrilo-1-phenyl-1-propenyl]-4-pyridinylidene}-2-phenylethylidene]-1-pyridinyl}-3-phenyl-2-propenenitrile (**4**). The reaction was followed by IR and ^{1}H NMR spectroscopy and thin-layer chromatography (neutral Al_2O_3, ethyl acetate as the eluent). The product is a polyconjugated system containing two *N*-(2-cyano-1-phenylvinyl)-1,4-dihydropyridine fragments bonded by a 1-cyano-2-phenyl-1,3-butadiene bridge (Scheme 1).

Bis(dihydropyridine) **4** is a black powder (m.p. 142–144 °C) that is soluble in chloroform, acetone, ethyl acetate, acetonitrile, dioxane, and DMSO. The solutions are opaque and black or transparent and dark red at low concentrations. In concentrated sulfuric and hydrochloric acids the adduct **4** forms transparent brown solutions of the corresponding salts. The basicity of bis(dihydropyridine) **4** (pK_{aBH^+} = 5.09 in methanol), determined by potentiometric titration, is similar to that of pyridine (pK_{aBH^+} = 5.37 in methanol).[11] Neutralization of the hydrochloric solution of **4** with aqueous concentrated NaOH resulted in a black precipitate (m.p. 170–185 °C). Its IR spectrum consists of broad absorption bands for the double bonds and cyano groups at 3050 ($\nu_{H-C=}$), 2210–2170 (ν_{CN}), and 1630 cm^{-1} ($\nu_{C=C}$). The ^{1}H NMR spectrum contains a broad, intense

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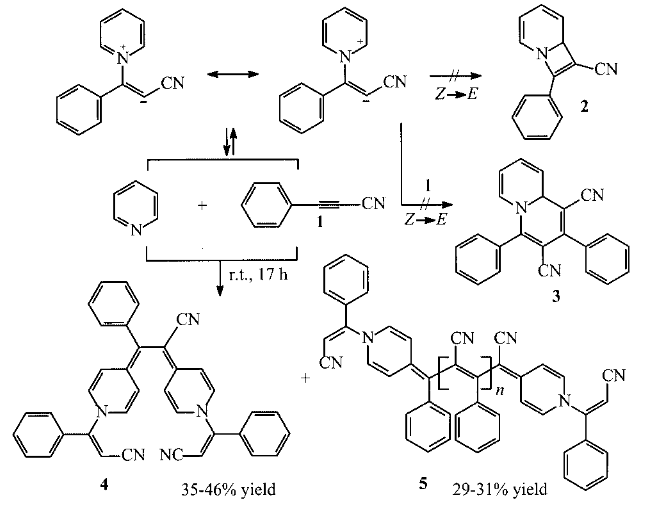

Scheme 1.

signal at δ = 8.00–6.90 ppm and very weak broad signals at δ = 6.76–6.23, 5.17, 4.81, and 2.50–1.90 ppm. The appearance of the spectrum is indicative of oligomeric structures like **5**, **7**, and **8** (see below). The signals at δ = 2.50–1.90 ppm likely belong to the tetrahydropyridine moieties of structure **8**.

Bis(dihydropyridine) **4** is paramagnetic: the EPR spectrum contains a symmetrical singlet with N = 4.5×10^{17} spin/g, ΔH = 0.84 mT, and g = 2.0031 [after heating in vacuo at 155–175 °C (2 Torr) for 2 h, N = 1.2×10^{18} spin/g, ΔH = 0.60 mT]. The electrical conductivity of adduct **4** is 1.4×10^{-13} Cm cm^{-1} (tablet). These values are typical of undoped polyvinylenes[12] and likely originate from higher oligomers **5** and **8** that form from adduct **4** over time.

The ratio of starting reagents has a pronounced effect on the yield of bis(dihydropyridine) **4**. When the molar ratio of pyridine/acetylene **1** was 12:1, the adduct **4** was obtained in 35–46% yield, whereas a reduction of pyridine content in the reaction mixture (for example, pyridine/**1** = 4:1, 2:1, 1:1, 1:5) leads to a decrease of the yield of adduct **4**, and some acetylene **1** remains unreacted. It follows that pyridine, as a base, participates in the intermediate stabilization and proton-transfer steps. Indeed, in diethyl ether, chloroform, or *tert*-butyl alcohol a significant increase of the reaction time (up to two weeks and longer) was observed. The same occurs at reaction temperatures of between –25 and –10 °C.

Along with bis(dihydropyridine) **4**, the reaction affords higher oligomer **5** (soluble in ethyl acetate, ca. 30% yield), which is terminated by *N*-(2-cyano-1-phenylvinyl)-1,4-dihydropyridine moieties (Scheme 1). These products can be separated by column chromatography (neutral Al_2O_3, ethyl acetate as the eluent).

The structure of bis(dihydropyridine) **4** was established by ^{1}H, ^{13}C, ^{15}N, and 2D (NOESY, COSY, HSQC, HMBC) NMR, IR, and UV spectroscopy. Its molecular mass was determined by the MALDI-TOF method.

Two narrow singlets (δ = 5.22 and 4.88 ppm, 2 H) can be seen in the ^{1}H NMR spectrum of the bis(dihydropyridine) derivative **4** for the olefinic protons of the *N*-(2-cyano-1-phenylvinyl) groups. The protons of the 1,4-dihydropyridine rings appear as two sets of doublets at δ = 6.59, 6.49, 6.28, and 5.85 (4 H) and 6.82, 6.75, 6.67, and 5.99 (4 H) ppm. A multiplet in the region of δ = 7.70–7.30 ppm (15 H) belongs to the phenyl substituents. The absence of the 4-H hydrogen atom signal, which should be observed as a multiplet due to interaction with the hydrogen atoms at the positions 3 and 5 of the dihydropyridine ring, points to a 4-methylene-1,4-dihydropyridine structure. According to the ^{13}C NMR spectrum, the adduct **4** has quaternary C-4 and C-4′ carbon atoms and this is supported by the HSQC spectrum, which shows no cross-peaks with the signals of these nuclei (Figure 1).

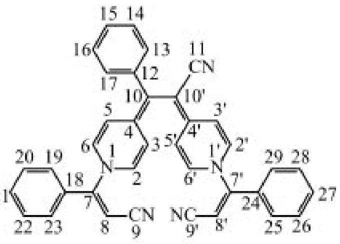

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Figure 1. Hydrogen and carbon numbering of bis(dihydropyridine) **4**.

The 1D ^{15}N NMR spectrum of adduct **4** shows signals for the nitrogen atoms in cyano groups at δ = –106.90 (position 9′), –109.68 (position 9), and –121.49 (position 11) and those in dihydropyridine cycles at δ = –231.20 (N-1′) and –237.40 (N-1) ppm (Figure 1). The positions 1, 1′, 9, and 9′ were assigned by a 2D ^{1}H-^{15}N HMBC experiment.

The configuration of the terminal cyanoethenyl groups (positions 9 and 9′) in the adduct **4** was also determined by a 2D NMR technique. Thus, in the (^{1}H, ^{1}H) NOESY spectrum, cross-peaks of olefinic (8-H and 8′-H) and *ortho*-phenyl hydrogens are observed, but there is no correlation between the olefinic and *ortho*-dihydropyridine hydrogen atoms. This indicates a *Z*-configuration of the *N*-(2-cyano-1-phenylvinyl) groups (Figure 2). The NOESY spectrum also shows a cross-peak between the signals of dihydropyridine hydrogen 5-H and the phenyl *ortho*-hydrogen (Figure 2).

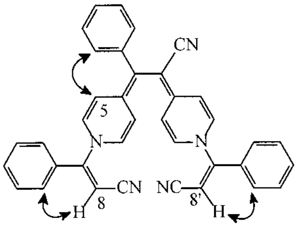

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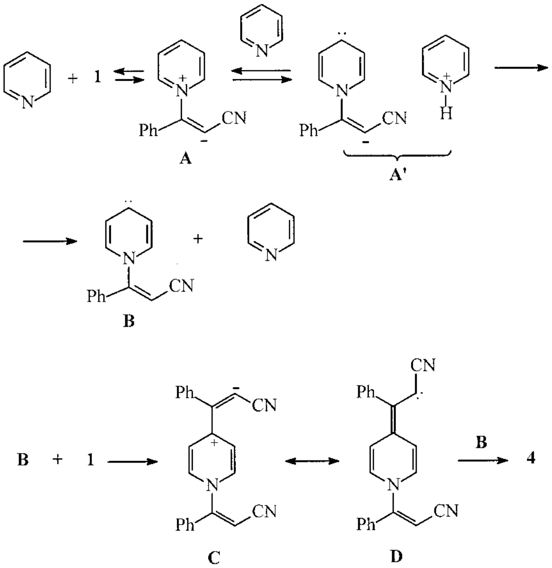
Figure 2. Cross-peaks in the NOESY spectrum of bis(dihydroxypyridine) **4**.

The IR spectrum (KBr) of **4** shows broad maxima at 2208, 2188, and 2176 cm^{-1} corresponding to the C≡N stretches. The C=C stretches are observed in the regions of 1648 and 1605–1580 cm^{-1}. The bands at 3059 and 3027 cm^{-1} are assigned to the =C–H stretches of the olefinic, phenyl, and dihydropyridine moieties. The corresponding deformations are found at 1418, 1327, 1267, 1210, 1180, 1151, 991, 836, 762, and 699 cm^{-1}. The band at 1359 cm^{-1} is assigned to the stretching of the C–N bonds of the dihydropyridine rings.[13–15] The IR spectra of **4** in paraffin oil and chloroform do not contain absorption bands for the NH moieties.

The UV spectrum of **4** in ethanol shows two relatively narrow absorption bands with maxima at 274 and 344 nm and a broad band at 463 nm (log ε = 4.77, 4.70, and 4.51, respectively). A comparison of the spectrum with that of a model compound (3-phenyl-2-propenenitrile, PhCH=CHCN, *E*/*Z* = 80:20) where a band is observed at 275 nm (ethanol), suggests that the two shorter-wavelength bands (274 and 344 nm) correspond to the $\pi \rightarrow \pi^*$ transitions in *N*-(2-cyano-1-phenylvinyl) groups, whereas the band in the visible region (463 nm) likely belongs to the entire polyconjugated bis(1,4-dihydropyridinylidene)-2-cyano-3-phenyl-1,3-butadiene system.[16]

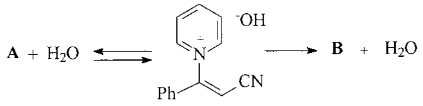
The IR spectrum of oligomer **5** contains a broad band at 2180–2160 cm^{-1} for the C≡N stretch and bands for the C=C and =C–H stretches at 3040, 1630, and 1570 cm^{-1}. Its UV spectrum (ethanol) contains bands with maxima at 265 and 407 nm. The ^{1}H NMR spectrum displays signals for the expected NCH$_2$CH$_2$C= unit (δ = 3.80–3.40 ppm), in the structure **8**, dihydropyridine rings (δ = 6.90–4.53 ppm, very weak), as well as broad and intense phenyl signals (δ = 7.80–7.00 ppm).

The assembly of adduct **4** is likely to start with nucleophilic attack of pyridine at the triple bond of acetylene **1**, which normally proceeds *anti*-stereospecifically to give an *E* anion.[17] The zwitterion **A** thus formed undergoes proton transfer, presumably pyridine-assisted (this explains the favorable effect of the excess pyridine), via the intermediate salt **A′** to give carbene **B**. The latter adds to the second molecule of acetylene **1** to form zwitterion **C**, which recombines (in carbenic form **D**) with another molecule of the carbene **B** to finally furnish the adduct **4** (Scheme 2).

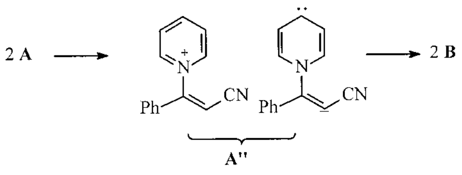


Scheme 2.

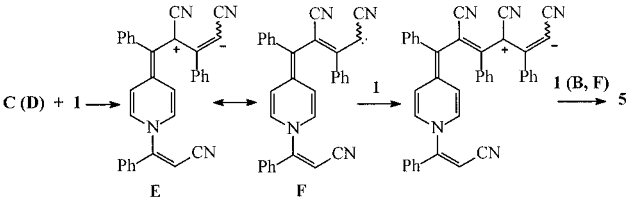
In these transformations, the proton-transfer agent may be trace amounts of water:



or another molecule of zwitterion **A** through the dimeric salt **A′′**:



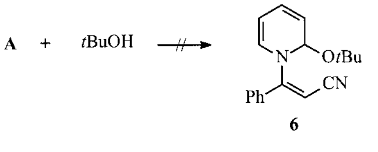
The interaction of intermediate **C** (**D**) with acetylene **1** results in oligomerization of the former via adducts of type **E** (**F**), which are stabilized by recombination with each other and with carbene **B** to afford oligomer **5** (Scheme 3).



Scheme 3.

None of the anticipated adducts were detected when the reaction was conducted in the presence of cyclohexene (20–25 °C, 18 h) or ethoxyethene (20–25 °C, 26 h) as carbene trappers, probably due to the nucleophilic character and extensive delocalization (hence low reactivity) of the postulated carbene **B**.

It is known that zwitterions formed from pyridine and dimethyl acetylenedicarboxylate can be trapped by benzaldehyde to give benzoyl fumarates,[18] substituted propargyl alcohols,[19] and benzylidenesuccinates.[20] However, our attempts to detect these zwitterionic intermediates in the reaction of pyridine with acetylene **1** using excess benzaldehyde (20–25 °C, diethyl ether, 7–24 h; toluene, 20 h; –10 to –20 °C, dimethoxyethane, 6 h; 50–60 °C, no solvent, 2 h) gave no trapped species. Likewise, in the presence of *tert*-butyl alcohol (20–25 °C, 6 h; 83 °C, 3 h) none of the expected *N*-vinyldihydropyridine (**6**) was discernible in the reaction mixture.



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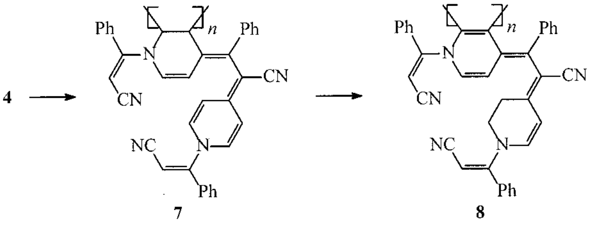
In all these cases only bis(dihydropyridine) **4** and the corresponding oligomer **5** were isolated, even when the reaction time was increased up to 50–70 h.

Bis(dihydropyridine) **4**, which is the major product of the reaction, appears to be unstable and gradually undergoes partial polymerization, even during its isolation. Evidently, the polymerization occurs across one of the double bonds of the dihydropyridine cycle and is accompanied by prototropic shifts. This process involves the formation of a polyene chain through the prototropic transformation of one of the dihydropyridine cycles to the tetrahydropyridine ones **7** and **8** (Scheme 4). The paramagnetic and semiconducting properties of adduct **4** may be explained by contamination with these oligomers.



Scheme 4.

The reaction (Scheme 2 and Scheme 3) was also monitored by UV, ^{1}H, ^{13}C NMR, and EPR spectroscopy. The UV absorption bands, signals of hydrogen or carbon atoms of the starting reagents (pyridine and acetylene **1**) in the NMR spectra, and the evolution of signals in the EPR spectra were used to track the reaction progress. The UV spectra of pyridine and acetylene **1** (ethanol) separately show absorption bands with a pronounced vibrational structure with maxima at 240, 245, 251, 257, and 261 nm (pyridine) and 248, 261, and 275 nm (acetylene **1**). Shortly (5 min) after mixing the starting reagents (pyridine/acetylene **1** = 12:1), an absorption band with a maximum at 341 nm appears whose intensity steadily increases, and after 10 min a shoulder at 392 nm is observed. These bands do not belong to adduct **4** and may be assigned to zwitterion **A** and the intermediates **B**–**F**. Over the following 2 h the intensities of the bands at 341 and 392 nm gradually increase and a new band related to the oligomer **5** appears at 463 nm. After 15 h the vibrational structure of the bands of the starting materials in the region of 240–270 nm has disappeared, along with the band at 392 nm, and maxima at 277 and 344 nm for the adduct **4** are discernible. After 20 h the absorption bands of adduct **4** at 274, 344, and 463 nm dominate the spectrum (Figure 3).

Likewise, when the starting reagents are mixed in an NMR tube ($CDCl_3$, pyridine/acetylene **1** = 12:1), after 15 min the ^{1}H NMR spectrum shows signals of the starting reagents only (δ = 8.58–7.21 ppm). After 1 h, three groups of new signals of low intensity appear at δ = 7.17 (t), 7.10 (d), and 7.02 (m) ppm. Correspondingly, in the ^{13}C NMR spectrum signals at δ = 139.15, 124.58, 120.35, and 112.97 ppm are observed. These signals are assignable to the phenyl substituents of the intermediates **A**–**F**. Vinyl hydrogen signals (δ = 5.22 and 4.88 ppm) and those of dihydropyridine moieties (δ = 6.82, 6.75, 6.67, 6.59, 6.49, 6.28, 5.99, and 5.85 ppm) become discernible only after 96 h (the reaction proceeds significantly slower in $CDCl_3$) with simultaneous decrease of the intermediates' signals (δ = 7.17, 7.10, and 7.02 ppm). The signals of the adduct **4** gradually increase with time.

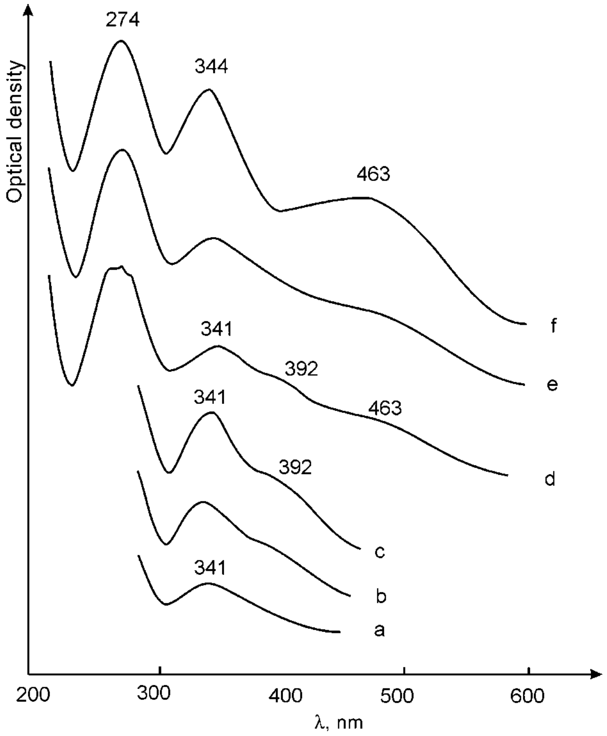


Figure 3. Evolution of UV patterns in the reaction of pyridine with phenylcyanoacetylene **1** (pyridine/acetylene **1** = 12:1, 20–22 °C): a) 5 min, b) 10 min, c) 2 h, d) 10 h, e) 15 h, f) 20 h.

In the EPR spectrum of the reaction mixture of pyridine and acetylene **1** (12:1), a weak signal tentatively assigned to the adduct **4** or its oligomers **5**, **7**, and **8** appears in the region of g = 2.0030 after 1–1.5 h. The intensity of the signal gradually increases and during the following 17 h no other signals are observed.

Conclusions

A new approach to the synthesis of functionalized polyconjugated 1,4-dihydropyridine systems has been found and illustrated by the reaction of pyridine with phenylcyanoacetylene. It can be used for the design of organic conductors, optoelectronic materials, and biologically active compounds. The scope and limitations of this reaction are now being investigated by us with substituted pyridines and arylcyanoacetylenes with positive preliminary results. No obvious fundamental reasons are envisaged as to why this reaction might be limited to this first example.

Experimental Section

IR spectra were measured on Specord IR 75 and IFS 25 instruments (in KBr). UV/Vis spectra were measured on a Perkin–Elmer Lambda 35 instrument at room temp. (EtOH, d = 0.1 cm). ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded with a AV-400 Bruker BioSpin spectrometer (400, 100, and 40.5 MHz respectively) in $CDCl_3$

with HMDS as an internal standard. Column and thin-layer chromatography was carried out on neutral Al_2O_3 (with ethyl acetate as eluent). EPR spectra were obtained with a SE/X-2547 spectrometer (Radiopan, Poland). MALDI-TOF mass spectra of the bis(dihydropyridine) derivative **4** were obtained with a Voyager DE spectrometer from PerSeptive Biosystems Inc., USA. The specific dark conductivity was measured using a VK 2-16 electrometric amplifier and an E6-13A teraohmmeter. Phenylcyanoacetylene (**1**) and the model compound 3-phenyl-2-propenenitrile (E/Z = 80:20) were prepared according to known procedures.[21,22]

(*Z*)-3-[4-(1-Cyano-2-{1-[(*Z*)-3-nitrilo-1-phenyl-1-propenyl]-4-pyridinylidene}-2-phenylethylidene)-1-pyridinyl]-3-phenyl-2-propenenitrile (4) and Oligomer 5: A mixture of pyridine (5.70 g, 72 mmol) and phenylcyanoacetylene **1** (0.76 g, 6 mmol) was stirred at 20–25 °C for 17 h. The unreacted pyridine was then removed in vacuo and the viscous residue was washed with hexane. The black powder formed was dried in vacuo to give 1.26 g of the product containing the adduct **4** and oligomer **5**, m.p. 150–165 °C. The products can be separated by two methods (**A** or **B**).

Method A: The crude product (1.26 g) was dissolved in ethyl acetate and chromatographed on a column with neutral Al_2O_3 (ethyl acetate as eluent). The procedure was repeated seven times to afford 0.44 g (35%) of bis(dihydropyridine) **4** as a black powder, m.p. 142–144 °C (ethyl acetate) and 0.40 g (31%) of oligomer **5** as a dark-brown powder, m.p. 130–170 °C.

Method B: The crude product (1.26 g) was washed with diethyl ether (20 × 20 mL). The diethyl ether was removed in vacuo and the residue was chromatographed on a column with neutral Al_2O_3 (ethyl acetate as eluent) to give 0.32 g of the bis(dihydropyridine) derivative **4**. The residue that was insoluble in diethyl ether, which contains oligomer **5** and remaining **4**, was separated by column chromatography to afford an additional 0.26 g of adduct **4** as a black powder, m.p. 142–144 °C (ethyl acetate) and 0.36 g (29%) of oligomer **5** as a dark-brown powder, m.p. 130–170 °C. Total yield of bis(dihydropyridine) **4** was 0.58 g (46%).

Bis(dihydropyridine) 4: M.p. 142–144 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.70–7.30 (m, phenyl substituents), 6.82 (dd, $^{3}J_{2',3'}$ = 7.9, $^{4}J_{2',6'}$ = 1.8 Hz, 1 H, 2′-H), 6.75 (dd, $^{3}J_{5',6'}$ = 8.0, $^{4}J_{2',6'}$ = 1.8 Hz, 1 H, 6′-H), 6.67 (dd, $^{4}J_{3',5'}$ = 2.4 Hz, 1 H, 3′-H), 6.59 (dd, $^{3}J_{2,3}$ = 8.3, $^{4}J_{2,6}$ = 1.9 Hz, 1 H, 2-H), 6.49 (dd, $^{3}J_{5,6}$ = 8.4, $^{4}J_{2,6}$ = 1.9 Hz, 1 H, 6-H), 6.28 (dd, $^{3}J_{5,6}$ = 8.4 Hz, 1 H, 5-H), 5.99 (dd, $^{3}J_{5',6'}$ = 8.0 Hz, 1 H, 5′-H), 5.85 (dd, $^{4}J_{3,5}$ = 2.3 Hz, 1 H, 3-H), 5.22 (s, 1 H, 8′-H), 4.88 (s, 1 H, 8-H) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 158.01 (C-7′), 157.69 (C-7), 142.60 (C-4′), 133.97 (C-18), 133.11 (C-24), 132.37 (C-27), 132.15 (C-6′), 131.84 (C-2′), 131.70 (C-21), 129.92 (C-2), 129.61 (C-12), 129.48 (C-29), 129.48 (C-25), 129.35 (C-6), 129.20 (C-23), 129.20 (C-19), 129.15 (C-16), 129.15 (C-14), 128.82 (C-22), 128.82 (C-20), 128.70 (C-4), 128.57 (C-28), 128.57 (C-26), 128.45 (C-17), 128.45 (C-13), 126.73 (C-15), 120.78 (CN, C-11), 116.72 (CN, C-9′), 115.65 (C-10), 115.46 (CN, C-9), 113.51 (C-3), 113.46 (C-3′), 112.28 (C-5), 111.53 (C-5′), 90.00 (C-10′), 85.13 (C-8′), 79.92 (C-8) ppm (see Figure 1 for carbon numbering). The IR, UV, and ^{15}N NMR spectra of the bis(dihydropyridine) **4** are described and discussed in the main text. MALDI-TOF-MS [positive ions, matrix: 2-cyano-3-(4-hydroxyphenyl)-2-propenoic acid (CHCA)]: m/z = 539.42 [M^+], 540.28 [M + H]$^+$, 541.36 [M + 2H]$^+$, 542.35 [M + 3H]$^+$. $C_{37}H_{25}N_5$ (539.64): calcd. C 82.35, H 4.67, N 12.98; found C 82.16, H 4.57, N 12.89.

Oligomer 5: M.p. 130–170 °C. The UV and ^{1}H NMR spectra are described and discussed in the main text. IR (KBr): $\tilde{\nu}$ = 3090, 2190–2160, 1640, 1580, 1550, 1480, 1440, 1410, 1360–1340, 1320, 1250, 1190, 1160, 1130, 1050, 1020, 980, 920, 840, 800, 760, 690, 530, 450 cm^{-1}. $C_{46}H_{30}N_6$: calcd. C 82.86, H 4.53, N 12.60; found C 82.10, H 4.09, N 12.18.

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