Electronic Supplementary Information
Bicycle pedal photoisomerization of 1-phenyl-4-(4-pyridyl)-1,3-butadienes in glassy isopentane at 77 K

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Electronic Supplementary Information: Materials and detailed synthetic procedures. Table with spectral characteristics and figures with additional spectra.

Materials. trans-Cinnamaldehyde (99%, Acros Organics), 4-picoline (98%, Sigma-Aldrich), acetic anhydride (Ac₂O) (certified ACS grade, Fisher Chemicals), ethynylbenzene (98%, Sigma-Aldrich), N-bromosuccinimide (NBS) (99%, Aldrich), AgNO₃ (crystal, ‘Baker Analyzed’ reagent, J.T. Baker Chemical Co.), 4-bromopyridine hydrochloride (98%, TCI America), trimethylsilylacetylene (98%, Alfa Aesar), Pd(PPh₃)₄ (98%, Sigma-Aldrich), CuI (98%, Sigma-Aldrich), HN(iPr)₂ (Eastman Kodak), CuCl (ACS reagent, Matheson, Coleman & Bell), NH₂OH•HCl (reagent plus, 99%, Sigma-Aldrich), 1-butanimine (n-BuNH₃) (99%, TCI America), 5% Pd/CaCO₃ (Pd, 5 wt% on CaCO₃, poisoned with lead, Sigma-Aldrich), quinoline (reagent ACS synthetic, Eastman Kodak), 4-pyridinecarbaldehyde (Aldrich), triphenylphosphoranylideneacetaldehyde (Aldrich), H₂ gas (ultrahigh purity grade, Air Products), acetic acid, glacial (ACS grade, EMD), NaOAc (‘Baker analyzed’ reagent, J. T. Baker Chemical Co.), Na₂SO₄ (anhydrous, low nitrogen, crystalline, powder, Mallinchnrodt), KOH (85+%, ACS reagent, Sigma-Aldrich), silica gel (silica gel 60, 230-400 mesh ASTM, particle size ~ 0.040-0.063 mm, from EMD), sand (white quartz, 50+70 mesh, Sigma-Aldrich), CH₂Cl₂ (Chromasolv plus, for HPLC, ≥ 99.9%, Sigma-Aldrich), ethyl acetate (EtOAc) (HPLC grade, Fisher), hexane (ACS grade, EMD), CDCl₃ (99.8 atom % D contains 0.03% (v/v)
TMS, Sigma-Aldrich), acetone (AR®, ACS grade, Mallinckrodt), methanol (ACS grade, EMD), benzene (Omnisolv, suitable for spectrophotometry, EMD), THF (ACS grade, EMD), CHCl₃ (HPLC grade, EMD), ethyl ether, anhydrous (stabilized HPLC grade, Fisher), and isopropyl alcohol (BDH, meets ACS specifications, VWR international). Except for acetone which was distilled prior to use, these reagents were utilized in the syntheses as received.

Syntheses

1-Phenyl-4-(4-pyridyl)-trans-1,trans-3-butadiene¹: 4-Picoline (4.43 mL, 4.23 g, 45.4 mmol) and trans-cinnamaldehyde (5.72 mL, 6.0 g, 45.4 mmol) were added to a solution of AcONa (7.51 g, 91.6 mmol) in Ac₂O (65 mL) under N₂ gas and the reaction mixture was stirred at reflux for three days. It was then quenched with distilled water and extracted with CH₂Cl₂ (3×20 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated to give a crude semi solid. The crude compound was mixed with silica gel (5 g) and purified by chromatography on a silica gel (70 g) column using 1:3 hexane:EtOAc eluent to give 2.71 g (28.8%) of orange yellow crystals. ¹H NMR (300 MHz, CDCl₃)  8.55(d, 2H, J = 6.1 Hz), 7.47(d, 2H, J = 8.3 Hz), 7.36(t, 2H, J = 7.5 Hz), 7.29-7.26(m, 3H), 7.18-7.09(m, 1H), 7.01-6.92(m, 1H), 6.78(d, 1H, J = 15.3), 6.58(d, 1H, J = 15.3).

2-Bromoethynylbenzene²: Silver nitrate (10 mg, 0.06 mmol) and NBS (3.65 g, 20.5 mmol) were added to freshly distilled acetone (40 mL) in a round bottom flask at rt and stirred for 10 min. Ethynylbenzene (2 mL, 1.86 g, 18.2 mmol) was added dropwise to this mixture with a syringe under N₂. After stirring at rt under N₂ overnight, the reaction mixture was concentrated and distilled water was added to it. This aqueous mixture was extracted with hexane (2×20 mL) and the hexane layers were combined. The hexane solution was dried over anhydrous Na₂SO₄ and concentrated to give 2.9 g (88%) of the product as a viscous yellow liquid, whose ¹H NMR spectrum was sufficiently clean for use in the synthesis of cc-PPyB (see below). ¹H NMR (300 MHz, CDCl₃)  7.49-7.41(m, 2H), 7.37-7.27(m, 3H).

4-[2-(Trimethylsilyl)ethynyl]pyridine: To 150 mL of THF in a round bottom flask at -78 °C was added 4-bromopyridinium chloride (3.0 g, 15.4 mmol), Pd(PPh₃)₄ (0.9 g, 0.78 mmol, 5 mol %) and CuI (285 mg, 1.5 mmol, 10 mol %), followed by 15 mL of (iPr)₂NH. After out-gassing with three vacuum/N₂ gas flush cycles, trimethylsilylacetylene (3.25 mL, 2.24 g, 22.8 mmol) was added slowly with constant stirring under N₂ and the reaction mixture was allowed to stir at rt for 5 h. All steps were performed in the dark, under red light. The reaction mixture was filtered through a silica gel plug and the filtrate was concentrated to give the crude product. Chromatography through a silica gel (65 g) column using 1:5 EtOAc:hexane eluent gave 2.0 g (yield of
74%) of the pure compound. $^1$H NMR (300 MHz, CDCl$_3$) 8.56 (d, 2H, $J = 5.9$ Hz), 7.30 (d, 2H, $J = 5.9$ Hz), 0.26 (s, 9H).

4-Ethynlypyridine: 4-[2-(Trimethylsilyl)ethynyl]pyridine (2.0 g, 11.4 mmol) was dissolved in MeOH:CH$_2$Cl$_2$ (20 mL:10 mL), KOH (1.3 g, 23.2 mmol) pellets was added and the reaction mixture was stirred at rt for 3.5 h. It was then quenched with 20 mL of distilled water and extracted with CH$_2$Cl$_2$ (3×20 mL). The combined CH$_2$Cl$_2$ fractions were dried over anhydrous Na$_2$SO$_4$ and filtered through a short silica gel column (1.5 cm o.d. by 3 cm ht.) and chased with 40 mL of CH$_2$Cl$_2$. Removal of the CH$_2$Cl$_2$ by rotary evaporation yielded 1.3 g of pale yellow product, which was used in the next step although slightly contaminated with EtOAc. All operations were carried out in the dark. $^1$H NMR (300 MHz, CDCl$_3$) 8.6(d, 2H, $J = 5.6$), 7.35(d, 2H, $J = 5.6$), 3.29(s, 1H).

1-Phenyl-4-(4-pyridyl)-1,3-butadiyne: n-Butyl amine (2.6 g, 35.5 mmol), 4-ethynlypyridine (1.3 g, 12.6 mmol), copper (I) chloride (0.17 g, 1.73 mmol), and hydroxylamine hydrochloride (0.25 g, 3.6 mmol) were added in rapid succession to a mixture of MeOH (5 mL) and H$_2$O (5 mL) in an ice bath in the dark. 4-Bromophenylacetylene (2.1 g, 11.6 mmol) in 5 mL of MeOH was then added slowly and the reaction mixture was allowed to stand for 5 min at 0 °C in the dark and then stirred overnight at rt. To ensure that Cu(I)Cl maintain its +1 oxidation state, a total 1.0 g of NH$_3$OH•HCl was added slowly over 40 min. The reaction mixture, a viscous yellow liquid (after overnight stirring), was quenched with 15 mL of distilled water, followed by 50 mL of saturated aq. NH$_4$Cl, and stirred for 10 min. It was then extracted with ethyl ether (2×20 mL), EtOAc (2×20 mL) and CHCl$_3$ (2×20 mL), the combined organic layers were washed with 50 mL of brine solution, dried over anhydrous Na$_2$SO$_4$ and concentrated to give 2.4 g of crude product. Chromatography on a silica gel (~65 g) column, using CH$_2$Cl$_2$ and CHCl$_3$ as the initial and final eluent, respectively, gave 0.9 g (31%) of the pure enyne product. $^1$H NMR (300 MHz, CDCl$_3$) 8.62(d, 2H, $J = 5.1$ Hz), 7.4(d, 4H, $J = 4.3$ Hz), 7.35-7.27(m, 3H), 6.86(t, 1H), 6.73-6.62(m, 2H), 6.47(d, 1H, $J = 11.4$ Hz), see Figure 1S. In subsequent purifications chromatography on silica gel led to isomerization of cis-PPyB.

1-Phenyl-4-(4-pyridyl)-cis-1,cis-3-butadiene: 1-Phenyl-4-(4-pyridyl)-1,3-butadiyne (0.1 g, 0.49 mmol) and 5% Pd/CaCO$_3$ (0.022 g), poisoned with Pb and α-quinoline, were dissolved in 3:1 MeOH:EtOAc solvent mixture in a 10 mL round bottom flask. (EtOAc was required for solubility purposes.) A balloon filled with H$_2$ was attached to the flask and the reaction mixture was stirred continuously at rt overnight. The balloon was removed and stirring was continued for 10 min under open air to remove excess H$_2$ gas. The solution was concentrated and the residue was chromatographed on a silica gel (60 g) column using 3:1 hexane:EtOAc eluent to give 0.05 g (yield of 51%) of pure product. $^1$H NMR (300 MHz, CDCl$_3$) 8.6(d, 2H, $J = 5.1$ Hz), 7.4(d, 4H, $J = 4.3$ Hz), 7.35-7.27(m, 3H), 6.86(t, 1H), 6.73-6.62(m, 2H), 6.47(d, 1H, $J = 11.4$ Hz), see Figure 1S. In subsequent purifications chromatography on silica gel led to isomerization of cc-PPyB.
Figure 1S. $^1$H NMR spectrum of cc-PPyB in CDCl$_3$, Bruker 300 MHz spectrometer from the initial silica chromatography.

Pure cc-PPyB was obtained by column chromatography on wet packed alumina using a 3:1 mobile phase of hexane:ethyl acetate.

$trans$-3-(4-Pyridyl)propenal$^5$: A reaction mixture consisting of 4-pyridinecarbaldehyde (0.85 g, 7.5 mmol) and triphenylphosphoranylideneacetaldehyde (2.63 g, 8.65 mmol) in benzene (100 mL) was heated under reflux for 24 h under inert conditions. After solvent evaporation, extraction of the solid residue with ice-cooled ether allowed partial separation of the 3-(4-pyridyl)propenal isomers from the less soluble (C$_6$H$_5$)$_3$P=O. Minimizing the presence of triphenylphosphine oxide is essential as column chromatography failed to separate it from the desired $trans$-3-(4-pyridyl)propenal product. Column chromatography on silica gel using 3:2 hexane:ethyl acetate eluent yielded the $trans$-3-(4-pyridyl)propenal contaminated with triphenylphosphine oxide. Pure $trans$-3-(4-pyridyl)propenal was obtained by multiple extractions with cold ether and filtrations of the precipitated triphenylphosphine oxide. $^1$H NMR spectroscopy confirmed the identity of the $trans$-3-(4-pyridyl)propenal which was used in the next step.
1-Phenyl-4-(4-pyridyl)-cis-1,trans-3-butadiene\textsuperscript{6}: Lithium hydroxide (0.425 g, 1.5 mmol) was added to a stirred solution of benzyltriphenylphosphonium salt (3.515g, 1.2 mmol) isopropyl alcohol (10 mL). After a few minutes of stirring, trans-3-(4-pyridyl)propenal (0.9 g, 6.76 mmol) was added and stirring was continued overnight. The initially opaque solution turned clear. The reaction was quenched with water and extracted with ethyl acetate. After solvent removal, the residue was chromatographed on silica gel using diethyl ether eluent. The refrigerated 1-phenyl-4-(4-pyridyl)-cis-1,trans-1,3-butadiene sample turns reddish brown on standing. It was, therefore, necessary to freshly chromatograph it prior to each fluorescence experiment.

1-Phenyl-4-(4-pyridyl)-trans-1,cis-3-butadiene\textsuperscript{7}: Irradiation of 1.09 \times 10^{-4} M benzene solution (~300 mL) of 1-phenyl-4-(4-pyridyl)-trans-1,trans-3-butadiene, under Ar-bubbling, with a 550 W Hanovia (Ace Glass) medium pressure Hg lamp housed in a Pyrex probe (\(\lambda > 300 \text{ nm}\)) yielded a tc-PPyB/\(tt\)-PPyB photostationary state rich in the tc-PPyB isomer. (Hexanes were substituted for benzene in a subsequent synthesis.) tc-PPyB is heat sensitive, therefore, no heating was applied in removing the benzene on the Buchi rotary evaporator. Chromatography on silica gel in the dark using 1:1 ethyl acetate:hexane eluent yielded pure tc-PPyB whose identity was confirmed by \(^1\)H NMR spectroscopy.\textsuperscript{8} As in the case of cc-PPyB, in subsequent purifications chromatography on silica gel led to decomposition of tc-PPyB. Pure tc-PPyB was obtained by column chromatography on wet packed alumina using a 3:1 mobile phase of hexane:ethyl acetate.

\textbf{Table 1S.} Absorption and emission properties of PPyB isomers in isopentane at 77 and 298 K.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Absorption</th>
<th>Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_{\text{max}}^{298}/\text{nm})</td>
<td>(\lambda_{\text{max}}^{77}/\text{nm})</td>
</tr>
<tr>
<td>(tt)-PPyB</td>
<td>326</td>
<td>333</td>
</tr>
<tr>
<td>(ct)-PPyB</td>
<td>311</td>
<td>-</td>
</tr>
<tr>
<td>(tc)-PPyB</td>
<td>311</td>
<td>324</td>
</tr>
<tr>
<td>(cc)-PPyB</td>
<td>302</td>
<td>312</td>
</tr>
</tbody>
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\(a\) Only the \(tt\)-PPyB values correspond to well resolved peaks.

The \(tc\)-PPyB \(\rightarrow\) \(tt\)-PPyB photoisomerization was also monitored by measuring fluorescence excitation spectra, Fig. 1S. The spectral matrix in Fig. 1S was obtained using \(tc\)-PPyB in the same IP glass that was used to obtain the fluorescence spectra in Fig. 4b of the paper. Because the excitation slit of the fluorometer exposes only a narrow...
horizontal band of the sample to the light, following the measurement of the fluorescence spectra, the NMR tube was moved vertically to expose a fresh band for the measurement of the fluorescence excitation spectra. That is why Fig. 2S is referred to as the companion spectral matrix of Fig. 4b of the paper.

![Fluorescence excitation spectra](image)

**Fig. 2S.** Fluorescence excitation spectra recorded in the course of the $tc$-PPyB $\rightarrow$ $tt$-PPyB by monitoring emission at 400 nm.

![Normalized Intensity](image)

**Fig. 3S** The green spectra are emissions from pure $tc$-PPyB in different IP glasses (two are from Fig. 4 – solid and dashed – and the other from Fig. 4S below – dotted). The blue line is emission from $tc$-PPyB obtained in situ by irradiation of $ct$-PPyB.
As shown in Fig. 4a,b of the manuscript, tc-PPyB gives emission with various degrees of structure presumably due to variation in IP glass microenvironments. The observed spectral variation is illustrated in Fig. 2S which includes tc-PPyB initial fluorescence spectra from different IP glasses. It can be seen that the spectra vary from almost structureless, as in Fig. 4b, to relatively structured as in Fig. 4a. Because of similarities between tt-PPyB emission and the solid blue or dotted green emission spectra in Fig. 2S, it was reasoned that if the structure in the tc-PPyB fluorescence spectra were due to tt-PPyB, subtraction of the latter should produce a relatively structureless tc-PPyB spectrum. The difference spectra in Fig. 4S show that subtraction of even unreasonably large percentages of tt-PPyB does not remove the vibronic structure.

Fig. 4S  a) Subtraction of photoproduct tt-PPyB (blue) from tc-PPyB (green) shown in black  b) Same as a), except with subtraction of the thermally obtained tt-PPyB (blue).

Results from an additional experiment (not included in the paper) are shown in Fig. 5S. The initial spectrum is the green dotted spectrum in Fig. 3S. As can be seen in the inset the spectral matrix is a two component system with tt-PPyB as the product. Here too, subtraction of the photoproduct spectrum by moving away from the tc-PPyB end on the normalization line in the inset of Fig. 5S does not yield a structureless spectrum.

Fig. 5S  tc-PPyB photoisomerization in a different IP glass at 77 K.

The different structural constraints imposed on the tc-PPyB starting material by differences in the IP cages are not only reflected in variation in the spectra in Fig. 3S.
They also control the geometry of the photoproduce as reflected in the different \textit{tt}-PPyB photoproduce emissions (compare the blue spectra in Fig. 6S). Fig. 6 in the manuscript clearly shows the initial formation of different \textit{tt}-PPyBs starting from the different \textit{tc}-PPyB IP glasses in Fig. 4. Starting from the two different \textit{tc}-PPyB spectra (green corners in the polygon), the reactions follow two entirely different trajectories via different \textit{tt}-PPyB intermediates towards the common final \textit{tt}-PPyB product.

**Fig. 6S** Enlarged version of Fig. 5: \textit{tc}-PPyB emission (green) and photoproduce \textit{tt}-PPyB emission (blue). Solid lines and dashed lines correspond to spectra from Figs. 5a and 5b in the manuscript, respectively.

**References**