JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

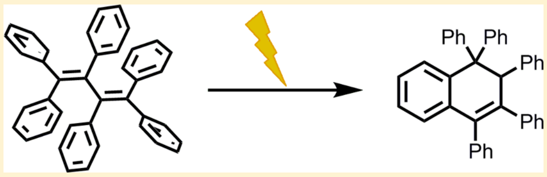
Photolability of Per-Arylated Butadienes: En Route to Dihydronaphthalenes

Jan Freudenberg,[†] Andrea C. Uptmoor,[†] Frank Rominger,[†] and Uwe H. F. Bunz*,[†,‡]

[†]Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
[‡]Centre of Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 225, 69120 Heidelberg, Germany

Supporting Information

ABSTRACT: Arylated butadienes were prepared employing transition-metal coupling techniques and characterized via UV/vis spectroscopy and X-ray crystal structure analysis. Identification of byproducts led to a photochemical route toward novel multiarylated dihydronaphthalenes. Arylbutadiene−dihydronaphthalene cyclization occurs in solution and in the solid state. Upon substitution of hexaphenylbutadiene, absorption is red-shifted and stability under ambient light is even more reduced.



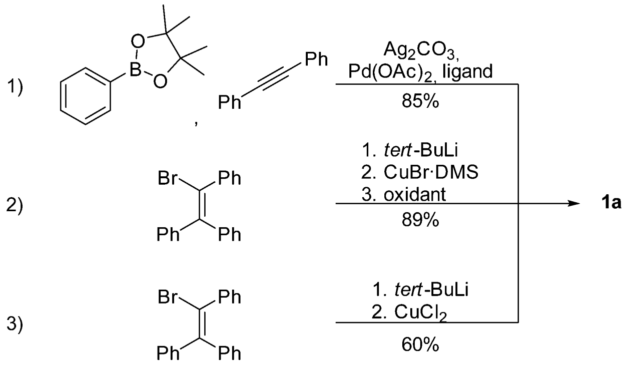
Herein, the photoreactivity of the light-sensitive arylated butadienes **1a**−**3a** is reported, leading to pentaarylated dihydronaphthalenes **1b**−**3b**.

Fluorophores exhibiting aggregation-induced emission (AIE) are attractive in optoelectronic applications, as chemical noses or biological probes.[1] In the aggregated state, strong fluorescence is observed due to restriction of intramolecular rotation, which allows relaxation of the excited state in solution.[2] Well-studied examples of AIE fluorophores are tetraphenylethenes (TPEs) and their derivatives.[3] An undisputed premise to apply AIE materials is their photostability. Zhu and co-workers demonstrated that TPE-based fluorophores undergo photocyclization into dihydrophenanthrenes, which are readily oxidized to phenanthrenes under aerobic conditions.[4] However, these characteristics should not affect device performance much, as such cyclization is fully reversible under anaerobic conditions.

Little is known about TPEs' higher homologues, the hexaaryl-butadienes. Do these materials exhibit AIE phenomena and are they sufficiently stable for applications? Very recently, aggregation-induced emission characteristics of hexaphenylbutadiene **1a**, a "second generation" emitter in luminescent solar concentrators (LSCs), were reported[5] but nothing is known about its photostability. Our group is interested in combining these attractive AIE properties with the possibility of further functionalization compared to TPEs to extend our portfolio of sensory materials.[6]

As we attempted to synthesize **1a** as a potential transport material for organic light-emitting diodes (OLEDs), employing a modified version of Miura's two-component reaction (Scheme 1, eq 1),[7] we observed a small singlet at approximately 4.5 ppm in the NMR spectrum. This impurity (<1%) formed independently of the method of preparation, as we tested Spring's coupling of vinyl bromide derivatives (Scheme 1, eq 2)[8] and developed our own protocol (eq 3; see Experimental Section for details).

Scheme 1. Synthetic Routes to Hexaphenylbutadiene 1a



Crystallization of "pure" **1a** from dichloromethane/methanol accidentally revealed the structure of the side product as dihydronaphthalene isomer **1b** (Figure 1).

Aryl-substituted butadienes undergo aryl vinyl photocyclizations under oxidative as well as nonoxidative conditions, leading to substituted phenyl naphthalenes[9] or dihydronaphthalenes.[10] To test our hypothesis of **1b** being a product of a photochemical 6-π-electron electrocyclization reaction, we irradiated **1a** at different wavelengths (250−419 nm) in cyclohexane under an inert atmosphere; formation of **1b**, occurring regardless of the wavelength irradiated, was monitored by GC/MS (Table 1). Stirring **1a** at reflux temperature in toluene or DMSO with or without a catalytic amount of toluenesulfonic acid did not induce reaction.

To the best of our knowledge, however, photocyclization of per-substituted 1,4-diphenylbutadienes with conformational flexibility at the butadiene moiety has never been reported. To broaden the scope of the photoreaction, we prepared the arylated butadienes **2a** and **4a** (Table 1). We could isolate **3a**

Received: October 7, 2014
Published: November 4, 2014

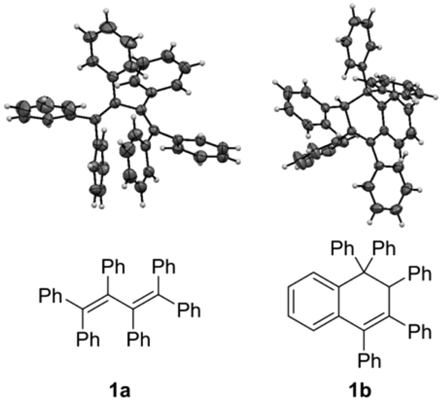
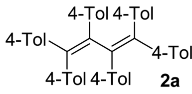
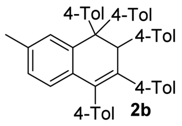
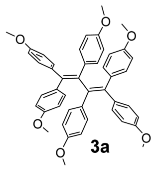
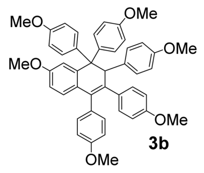
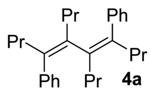
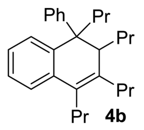


Figure 1. Crystal structures of compounds **1a** and **1b**.

Table 1. Photoreactions to Dihydronaphthalenes

Entry	Butadiene[a]	Cond.[b]	Product	Yield (%)[c]
1	**1a**	A	**1b**	95
2	**1a**	B	**1b**	70
3		A		99
4		A		98
5		C		–[d]

[a] 4-Tol: 4-tolyl. Pr: *n*-propyl. [b] A: N_2 atmosphere, toluene, 1 h, 350 nm. B: N_2 atmosphere, solvent-free, 34 h, 300 nm. C: N_2 atmosphere, toluene, 1 h, 300 nm. [c] Isolated yields. [d] Not observed.

employing brown-glass and red-light techniques. Miura et al. did not succeed in the isolation of **3a**; however, the authors obtained **3b** as the only thus far known example of this structural motif.[7] Compounds **1a**−**3a** were transformed into their cycloisomers **1b**−**3b** in excellent yields after irradiation in a photoreactor at λ = 350 nm (all structures were unambiguously confirmed by X-ray analysis). However, **4a** did not undergo cyclization to **4b**. After 1 h of irradiation at 300 nm and subsequent purification, only geometric (*E,E*)- and (*E,Z*)-isomers (1:2 ratio) could be detected via NMR. This result indicates that the aryl rings situated on the butadiene backbone are necessary for the cyclization reaction.

As gleaned from X-ray structure analyses (see Supporting Information and Figure 1), butadienes **1a**−**3a** are sterically overcrowded; the aryl rings are twisted out of the plane, and the butadiene backbone is pushed into a helical s-cis conformation. As comparable photocyclization reactions occur in fulgamides,[10e] which are forced into this s-cis geometry by a tether, the steric pressure in butadienes must enable the force behind the isomerization reaction.

Cyclization also occurs in the solid state under solvent-free conditions (50 mg scale, Table 1, entry 2). To further illustrate this reactivity, samples of **1a** and **1b** were dropcast on a TLC plate. After irradiation of **1a** with UV light (λ = 365 nm), the greenish emission of **1a** is replaced with the blue solid state fluorescence of **1b** (Figure 2).

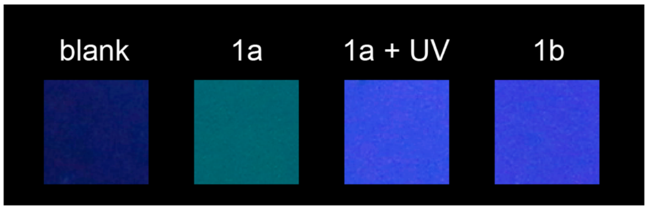


Figure 2. Photographs of compounds **1a** (before and after irradiation with a 3 W UV-LED at 365 nm) and **1b** dropcast on silica TLC plates under excitation with a hand-held UV-lamp at an emission wavelength of 365 nm. A blank TLC plate is shown as a reference.

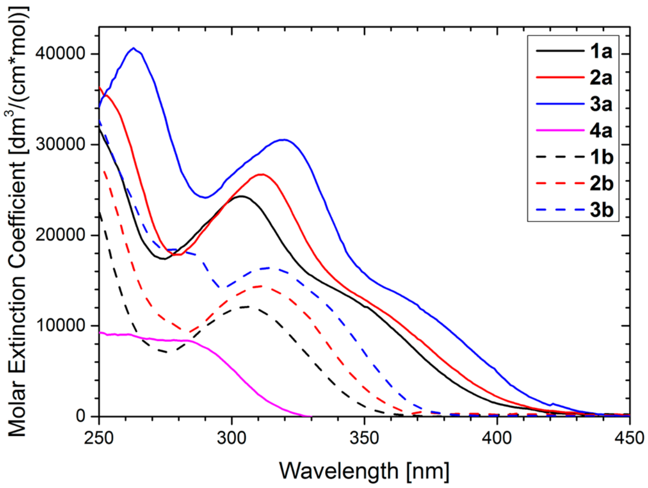


Figure 3. Molar absorption coefficient spectra of compounds **1**−**4** in dichloromethane.

UV/vis spectra (dichloromethane, Figure 3) illustrate the different absorptivities of **1a**−**4a** and **1b**−**3b**. Table 2 summarizes these data.

Substitution of the phenyl rings of **1a** (λ_{max} = 303 nm) with methyl or methoxy groups leads to an increasing red shift of the spectra thus rendering **2a** (λ_{max} = 312 nm) and **3a** (λ_{max} = 320 nm) even more photolabile to ambient light, as the absorption onset is further shifted into the visible regime and ambient light suffices to induce cyclization for **3a**. The same trend is observed for their isomerized counterparts **1b**−**3b**. As the dihydronaphthalenes absorb weakly from 350 to 400 nm, this range is ideal for the cyclization reaction, thus avoiding photobleaching of the products. In contrast, the absorption spectrum of **4a** differs from those of **1a**−**3a**. It does only exhibit a weak shoulder at 261 nm. Additionally, the onset of absorption is hypsochromically shifted by 90 nm and absorptivity is reduced. These results suggest that, although being bent out of the plane of the chromophore backbone in the solid state, the aromatic rings in the per-arylated species freely rotate in solution, allowing electronic communication with the chromophore backbone under extension of the delocalized π-system. This free rotation results in the very weak fluorescence of **1a**−**3a** in solution at room temperature, whereas rotation is hindered in the solid

Table 2. Optical Properties of Compounds 1−4 in Dichloromethane

	1a	2a	3a	4a	1b	2b	3b
λ_{max} [nm][a]	303	312	320	261[c]	306	310	314
Molar Extinction Coefficient [x 10^4 $dm^3/(cm*mol)$][b]	2.43	2.67	3.05	0.90[c]	1.21	1.44	1.64

[a] Absorption maximum peak refers to nearest absorption maximum in the absorption spectra to the solar spectrum threshold. [b] At λ_{max}. [c] Shoulder.

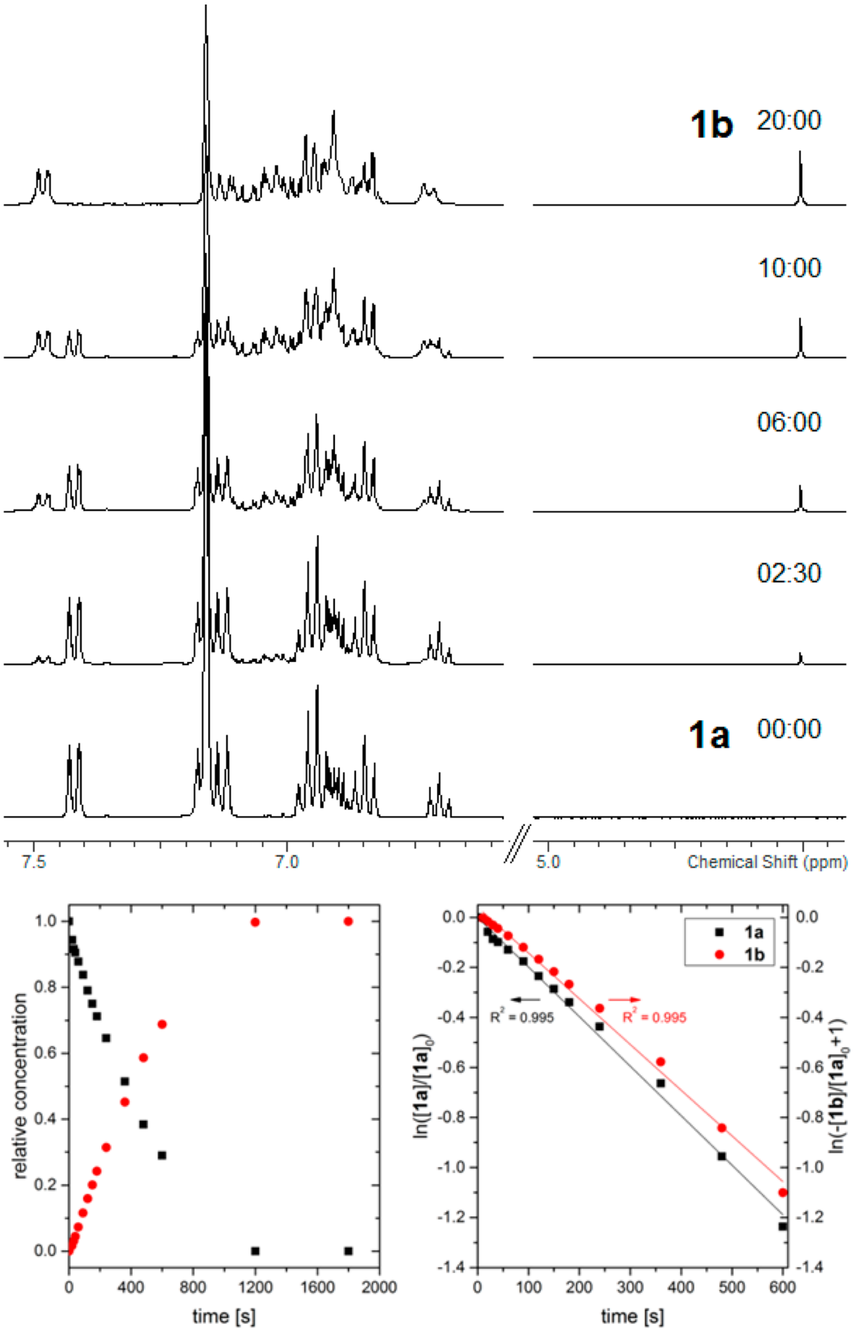
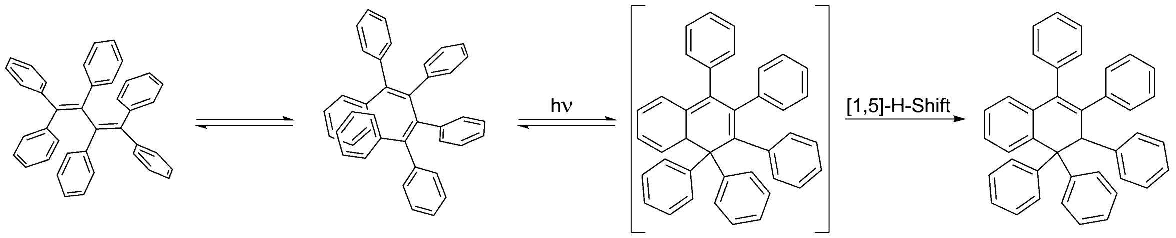


Figure 4. Top: Time-dependent monitoring [mm:ss] of the photocyclization reaction (λ = 350 nm) via NMR in benzene-d_6 under an inert atmosphere ([**1a**] = 22.9 mg/mL). Bottom left: Time-dependent relative concentrations (first 30 min) of **1a** and **1b** during the photoreaction in deuterated benzene. Bottom right: linearization and linear fit of [**1a**] and [**1b**]. [**1a**]$_0$ denotes the starting concentration.

state and greenish to yellowish aggregation-induced emission occurs (*vide supra*).

To gain further insight into the reaction, we performed a time-dependent NMR experiment in C_6D_6 ([**1a**] = 22.9 mg/mL) under an argon atmosphere. The sample was illuminated in a photoreactor at λ = 350 nm for different time intervals, and the composition was subsequently analyzed via NMR (Figure 4, top). (1) The photocyclization reaction proceeds smoothly, as no side products could be detected. (2) Photocyclization is fast; the reaction was complete in less than 20 min. (3) Under these reaction conditions, both the formation of **1b** and consumption of **1a** follow a first-order kinetic, assuming an excess of photons

Scheme 2. Photocyclization of 1a



1a **1a** **5** **1b**

is available. The data can be fitted employing Bodenstein's quasi-stationary principle (Figure 4, bottom right). This is in agreement with the mechanism of the reaction, which consists of a cyclization step and subsequent [1,5] hydrogen shift (Scheme 2).[11] (4) After an irradiation cycle, the formation of a deeply yellow to orange intermediate was observed, which disappeared quickly and can be ascribed to **5**.[10e]

In conclusion, per-arylated butadienes are photolabile, both in solution and in the solid state, rendering **1a**–**3a** less than ideal for long-term aggregation-induced emission applications, even under anaerobic conditions. Proceeding from these butadienes, we described a simple approach toward the synthesis of penta-arylated dihydronaphthalenes.

■ EXPERIMENTAL SECTION

All reagents and solvents were obtained from commercial suppliers and were used without further purification unless specified otherwise. Preparation of light sensitive materials was carried out employing brown glass and red-light techniques. Preparation of air and moisture sensitive materials was carried out in oven-dried flasks under an atmosphere of nitrogen or argon employing standard Schlenk techniques. Photocyclization reactions were carried out employing 3500, 3000, and 4190 Å light sources. ^{1}H NMR spectra were recorded at 298 K on a 300, 400, or 600 MHz spectrometer, and ^{13}C NMR spectra were recorded on a 75, 100, or 150 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and referenced internally to the solvent signal. Melting points are reported uncorrected. Infrared (IR) spectra are reported in wavenumbers (cm^{-1}) and were recorded neat. Photographs were taken under UV-light irradiation (λ = 365 nm) using a digital camera (objective: EF-S60 mm f/2.8 Macro USM). MS spectra were recorded using electron impact detected by magnetic sector and FT-ICR techniques, respectively. Absorption spectra were recorded in dichloromethane. Crystal-structure analysis was accomplished on diffractometers with Mo Kα radiation, λ = 0.71073 Å. Arylbutadienes **1a**, **2a**, and **4a** were prepared according to literature procedures.[7,8] Consequent exclusion of UV radiation and blue to yellow light resulted in the isolation of noncyclized **3a** instead of **3b**.[7]

1,1,2,3,4,4-Hexaphenyl-1,3-butadiene (1a). Under an argon atmosphere, 1,1′,1″-(2-bromo-1,1,2-ethenetriyl)tribenzene (300 mg, 895 μmol, 2.0 equiv) was dissolved in anhydrous diethyl ether (4 mL) and cooled to −78 °C. *tert*-Butyllithium (1.05 mL, 1.79 mmol, 1.7 M in pentane, 4.0 equiv) was added dropwise, and the mixture was allowed to stir at −78 °C for 1 h. Copper(II) chloride (120 mg, 895 μmol, 2.0 equiv) was added, and the reaction mixture was very slowly warmed to 45 °C and was stirred for additional 2 h. The reaction mixture was filtered through a plug of silica, eluting with a mixture of petroleum ether/diethyl ether 1:1. After removal of the solvents under reduced pressure, the crude product was subjected to column chromatography (silica, petroleum ether/diethyl ether 100:1), to yield the title compound as a slightly yellow solid (136 mg, 266 μmol, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (d, J = 7.4 Hz, 4 H), 7.06 (m, 12 H), 6.91–6.94 (m, 12 H), 6.87–6.89 (m, 2 H). Analytical data were in accordance with literature.[7]

1,1′,1′′,1′′′,1′′′′,1′′′′′-Buta-1,3-diene-1,1,2,3,4,4-hexayl-hexakis(4-methoxybenzene) (3a). The reaction and purification were performed in brown glassware and under red light. Under an inert gas atmosphere, to 1,2-bis(4-methoxyphenyl)ethyne (200 mg, 893 μmol, 1.0 equiv), (4-methoxyphenyl)boronic acid (191 mg, 1.28 mmol, 1.5 equiv), palladium(II) acetate (4.71 mg, 21.0 μmol, 2.5 mol %), silver(I) carbonate (231 mg, 839 μmol, 1.0 equiv), and tri-*p*-tolyl phosphate (7.73 mg, 20.1 μmol, 2.5 mol %) was added a mixture of 1-propanol/water (2.5 mL, 9:1). The reaction mixture was stirred at 120 °C for 30 min. The reaction mixture was allowed to cool to room temperature and was taken up in diethyl ether (50 mL) and water (50 mL), and insoluble materials were removed via filtration. The organic layer was washed thrice with water (50 mL) and dried over magnesium sulfate, and the volatiles were removed under reduced pressure. The crude product was subjected to column chromatography (silica, petroleum ether/ethyl acetate 5:1, R_f = 0.07) to yield the title compound as a yellow solid (171 mg, 248 μmol, 59%). Mp: 207–208 °C. IR (cm^{-1}): 3027, 3007, 2993, 2949, 2935, 2835, 1603, 1508, 1463, 1287, 1240, 1170, 1112, 1028, 826, 805, 773, 556. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.09 (d, J = 8.8 Hz, 4 H), 6.81–6.88 (m, 8 H), 6.59–6.62 (m, 8 H), 6.49 (d, J = 9.1 Hz, 4 H), 3.73 (s, 6 H), 3.71 (s, 6 H), 3.66 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.2, 158.1, 157.3, 140.6, 138.8, 137.4, 137.1, 134.4, 132.6, 132.6, 131.2, 113.0, 112.8, 112.6, 55.3, 55.2, 55.1. HRMS (EI (+)): m/z $[M]^{\bullet +}$calcd for $C_{46}H_{42}O_6$ 690.2981, found 690.2963. Elemental analysis calcd (%) for $C_{46}H_{42}O_6$: C, 79.98; H, 6.13. Found: C, 79.90; H, 6.34.

General Procedure for the Photocyclization Reaction (GP). Under a nitrogen atmosphere, the butadiene (200 μmol) was dissolved in thoroughly degassed toluene (25 mL) in a quartz flask. The solution was stirred for 1 h under UV-light irradiation (λ = 350 nm). The solvent was removed under reduced pressure, and the crude product was subjected to column chromatography (silica, petroleum ether) to yield the dihydronaphthalene. Recrystallization from dichloromethane/methanol yielded single crystals suitable for X-ray diffraction analysis.

1,1,2,3,4-Pentaphenyl-1,2-dihydronaphthalene (1b). GP was carried out with **1a** (102 mg, 200 μmol) in toluene (25 mL). Column chromatography (silica, petroleum ether, R_f = 0.10) yielded **1b** (97.0 mg, 190 μmol, 95%) as a colorless solid. *Solid State*: Under a nitrogen atmosphere, powdered **1a** (97.9 μmol) was added to a quarz flask equipped with a stirring bar and stirred without addition of solvent under UV light irradiation (λ = 300 nm) for 34 h. Purification via column chromatography on silica yielded **1b** as a colorless solid (68.5 μmol, 70%). Recrystallization from dichloromethane/methanol yielded single crystals with an identical unit cell as that for the crystals obtained after reaction in solution. Mp: 235–237 °C. IR (cm^{-1}): 3081, 3055, 3026, 3022, 1597, 1488, 1442, 1190, 1176, 1157, 1071, 1030, 999, 967, 911, 843, 793, 754, 722, 696, 637, 623, 585, 568. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28–7.51 (m, 3 H), 6.67–7.26 (m, 22 H), 6.62 (d, J = 7.2 Hz, 2 H), 6.48 (bs, 2 H), 4.35 (s, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.8, 143.4, 142.6, 139.7, 139.6, 139.4, 139.3, 138.5, 137.0, 131.1, 131.0 (bs), 130.9, 130.0, 129.6 (bs), 128.7, 128.1, 127.9 (bs), 127.6, 127.5 (bs), 127.5, 126.94, 126.87, 126.8, 126.6, 126.5 (bs), 126.3, 126.1, 60.0, 57.6. (Both ^{1}H and ^{13}C NMR spectra exhibit broad signals.) HRMS (EI (+)): m/z $[M]^{\bullet +}$ calcd for $C_{40}H_{30}$ 510.2348, found 510.2363.

7-Methyl-1,1,2,3,4-pentakis(4-methylphenyl)-1,2-dihydronaphthalene (2b). GP1 was carried out with **2a** (72.0 mg, 121 μmol) in toluene (15 mL). Column chromatography (silica, petroleum ether/

ethyl acetate 100:1, $R_f = 0.12$) yielded **2b** (71.0 mg, 119 μmol, 99%) as a colorless solid. Mp: 303−305 °C. IR (cm^{-1}): 3053, 3023, 2917, 2859, 1510, 1480, 1447, 1183, 1115, 1021, 843, 829, 820, 807, 786, 774, 767, 752, 740, 727, 718, 659, 626, 601, 585, 553, 536, 529, 509, 471. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.13−7.25 (m, 3 H), 7.01 (d, J = 8.4 Hz, 2 H), 6.88−6.97 (m, 3 H), 6.84 (d, J = 7.9 Hz, 2 H), 6.60−6.81 (m, 9 H), 6.54 (d, J = 8.1 Hz, 2 H), 6.36 (d, J = 6.8 Hz, 2 H), 4.19 (s, 1 H), 2.32 (s, 3 H), 2.28 (s, 3 H), 2.26 (s, 6 H), 2.24 (s, 3 H), 2.18 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 143.2, 141.0, 140.1, 140.0, 138.4, 137.1, 136.7, 136.3, 136.2, 136.09, 136.08, 135.8, 135.4, 135.3, 135.2, 131.2, 130.9 (bs), 130.6, 129.5 (bs), 128.63, 128.57, 128.3, 128.1, 127.1 (bs), 127.2, 127.1, 59.4, 57.5, 21.7, 21.4, 21.3, 21.2, 21.09, 21.06. (Both ^{1}H and ^{13}C NMR spectra exhibit broad signals.) HRMS (EI (+)): m/z [M]$^{\bullet+}$ calcd for C$_{46}$H$_{42}$ 594.3287, found 594.3271.

7-Methoxy-1,1,2,3,4-pentakis(4-methoxyphenyl)-1,2-dihydronaphthalene (3b). GP1 was carried out with **3a** (50.0 mg, 72.4 μmol) in toluene (8.4 mL). Column chromatography (silica, petroleum ether/ethyl acetate) yielded **3b** (49.0 mg, 70.9 μmol, 98%) as a colorless solid. ^{1}H NMR (300 MHz, CDCl3): δ 7.22 (d, J = 8.3 Hz, 2 H), 6.90 (d, J = 2.6 Hz, 1 H), 6.45−6.85 (m, 18 H), 6.37 (d, J = 7.3 Hz, 2 H), 4.14 (s, 1 H), 3.80 (s, 3 H), 3.76 (s, 3 H), 3.74 (s, 3 H), 3.72 (s, 6 H), 3.68 (s, 3 H). Analytical data were in accordance with literature.[7]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H, ^{13}C NMR spectra of **3a**, **1b**, and **2b** as well as the images of crystal structures for compounds **1a−3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail uwe.bunz@oci.uni-heidelberg.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a grant from the "Landesgraduiertenförderung (LGFG)".

■ REFERENCES

(1) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40*, 5361−5388. (b) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Commun.* **2009**, 4332−4353.

(2) Chen, J.; Law, C. C. W.; Lam, J. W. Y.; Dong, Y.; Lo, S. M. F.; Williams, I. D.; Zhu, D.; Tang, B. Z. *Chem. Mater.* **2003**, *15*, 1535−1546.

(3) (a) Dong, Y.; Lam, J. W. Y.; Qin, A.; Liu, J.; Li, Z.; Tang, B. Z.; Sun, J.; Kwok, H. S. *Appl. Phys. Lett.* **2007**, *91*, 11111−11113. (b) Tong, H.; Hong, Y.; Dong, Y.; Häussler, M.; Lam, J. W Y; Li, Z.; Guo, Z.; Guo, Z.; Tang, B. Z. *Chem. Commun.* **2006**, 3705−3707. (c) Chen, Q.; Zhang, D.; Zhang, G.; Yang, X.; Feng, Y.; Fan, Q.; Zhu, D. *Adv. Funct. Mater.* **2010**, *20*, 3244−3251. (d) Zhou, J.; Chang, Z.; Jiang, Y.; He, B.; Du, M.; Lu, P.; Hong, Y.; Kwok, H. S.; Qin, A.; Qiu, H.; Zhao, Z.; Tang, B. Z. *Chem. Commun.* **2013**, *49*, 2491−2493.

(4) Aldred, M. P.; Li, C.; Zhu, M.-Q. *Chem.—Eur. J.* **2012**, *18*, 16037−16045.

(5) Banal, J. L.; White, J. M.; Ghiggino, K. P.; Wong, W. W. H. *Sci. Rep* **2014**, *4*, 4635−4639.

(6) (a) Patze, C.; Broedner, K.; Rominger, F.; Trapp, O.; Bunz, U. H. F. *Chem.—Eur. J.* **2011**, *17*, 13720−13725. (b) Kumpf, J.; Bunz, U. H. F. *Chem.—Eur. J.* **2012**, *18*, 8921−8924. (c) Freudenberg, J.; Kumpf, J.; Schäfer, V.; Sauter, E.; Wörner, S. J.; Brödner, K.; Dreuw, A.; Bunz, U. H. F. *J. Org. Chem.* **2013**, *78*, 4949−4959. (d) Kumpf, J.; Freudenberg, J.; Schwaebel, S. T.; Bunz, U. H. F. *Macromolecules* **2014**, *47*, 2569−2573.

(7) Horiguchi, H.; Tsurugi, H.; Satoh, T.; Miura, M. *Adv. Synth. Catal.* **2008**, *350*, 509−514.

(8) Aves, S.; O'Connell, K.; Pike, K.; Spring, D. *Synlett* **2012**, *2012*, 298−300.

(9) (a) Fonken, G. J. *Chem. Ind. (London)* **1962**, 1327. (b) Baddar, F. G.; El-Assal, L. S.; Doss, N. A.; Shehab, A. H. *J. Chem. Soc.* **1959**, 1016−1020. (c) Baddar, F. G.; El-Assal, L. S.; Gindy, M. *J. Chem. Soc.* **1948**, 1270−1272.

(10) (a) Hart, R. J.; Heller, H. G.; Salisbury, K. *Chem. Commun.* **1968**, 1627−1628. (b) Srinivasan, R.; Merritt, V. Y.; Hsu, J. N. C.; op het Veld, P. H. G.; Laarhoven, W. H. *J. Org. Chem.* **1978**, *43*, 980−985. (c) Heller, H. G.; Strydom, P. J. *J. Chem. Soc., Chem. Commun.* **1976**, 50b−51. (d) Datta, P. K.; Yau, C.; Hooper, T. S.; Yvon, B. L.; Charlton, J. L. *J. Org. Chem.* **2001**, *66*, 8606−8611. (e) Krawczyk, K. K.; Madej, D.; Maurin, J. K.; Czarnocki, Z. *Tetrahedron: Asymmetry* **2011**, *22*, 1103−1107.

(11) Mallory, F. B.; Mallory, C. W. Photocyclizations of Stilbenes and Related Molecules. In *Organic Reactions*; Dauben, W. G., Boswell, G. A., Jr., Danishefsky, S., Gschwend, H. W., Heck, R. F., Hirschmann, R. F., Paquette, L. A., Posner, G. H., Reich, H. J., Eds.; John Wiley & Sons, Inc.: New York, 1984; pp 1−456.