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Synthesis, Crystal Structure, and Photophysical Properties of (1*E*,3*E*,5*E*)-1,3,4,6-Tetraarylhexa-1,3,5-trienes: A New Class of Fluorophores Exhibiting Aggregation-Induced Emission

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Abstract: Double Horner–Wadsworth–Emmons reaction of (*E*)-2,3-diaryl-1,4-bis(diethylphosphonyl)but-2-ene with (*p*-substituted) benzaldehydes gave (1*E*,3*E*,5*E*)-1,3,4,6-tetraarylhexa-1,3,5-trienes in moderate to good yields. Substitution of electron-withdrawing or -donating groups at the *para* position of the 1,6-diphenyl groups induced a slight bathochromic shift of UV spectra measured in $CHCl_3$ compared with that of the parent 1,3,4,6-tetraphenylhexa-1,3,5-triene. Although fluorescence was not observed with all the trienes in $CHCl_3$, they markedly emitted visible light in powder forms with quantum yields of 0.15–0.44. Introduction of amino groups at the *para* position of the 3,4-diphenyl groups induced a bathochromic shift of emission maxima with good solid-state quantum yields. Thus, the tetraarylated triene framework is found to serve as a new class of fluorophores that exhibit aggregation-induced emission.

Keywords: aggregation · chromophores · conjugation · fluorescence · materials science

Introduction

Since the pioneering report by Tang and co-workers,[1] growing interest has been paid to π-conjugated compounds, which exhibit aggregation-induced emission (AIE): an unusual phenomena in which nonemissive π-conjugated molecules in solution emit efficiently in the solid state, such as thin films, nanoparticles, powder, and crystals.[2] Efficient solid-state emission is essential for optoelectronic devices such as organic light-emitting diodes,[3] semiconductor lasers,[4] and solid sensors.[5] Therefore, exploration of novel AIE-active chromophores and understanding of their characteristics regarding molecular and electronic structures as well as three-dimensional alignment in the solid state are very important for the development of emitting materials employed in such optoelectronic devices.

In the course of our research on the stereoselective cross-coupling reaction of *gem*-diborylated compounds,[6] we observed that (1*E*,3*E*,5*E*)-1,3,4,6-tetraphenylhexa-1,3,5-triene (**1a**),[7] one of the products of the coupling reaction, was blue-fluorescent only in the powder form (Figure 1).[6b]

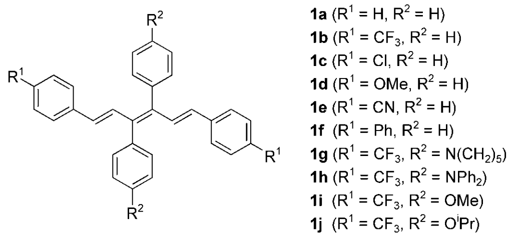

Figure 1. (1*E*,3*E*,5*E*)-1,3,4,6-Tetraarylhexa-1,3,5-trienes **1**.

Thus, **1a** was considered to be AIE-active. As (1*E*,3*E*,5*E*)-1,6-diarylhexa-1,3,5-trienes were reportedly less fluorescent in the solid state than in solution probably as a result of the formation of aggregates or an excimer,[8] it should be reasonable to attribute the observed AIE of **1a** to the presence of 3,4-diphenyl groups. Then, we turned our attention to (1*E*,3*E*,5*E*)-1,3,4,6-tetraarylhexa-1,3,5-trienes **1** as a new

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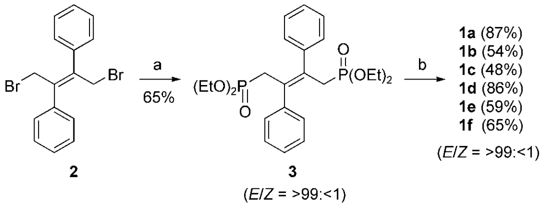
class of AIE-active fluorophores. Reported herein are the preparation, structures, UV absorption, solid-state fluorescence, and theoretical calculations of **1**.

Results and Discussion

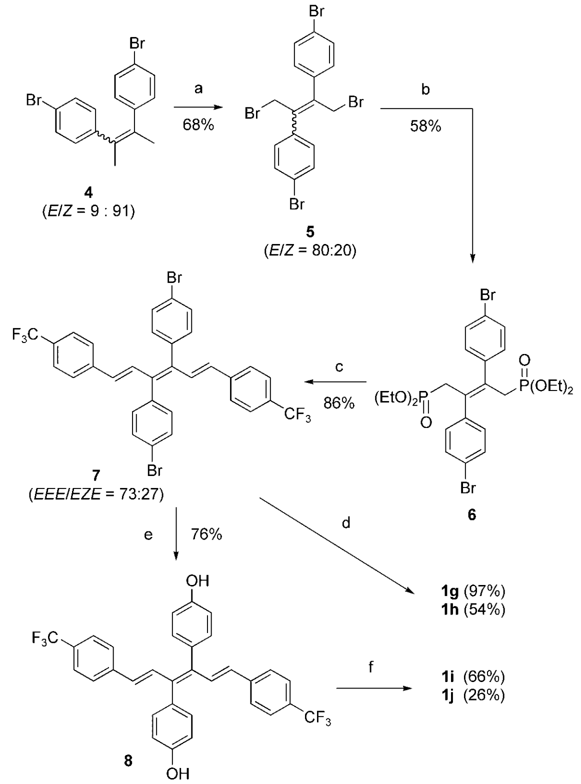
Preparation of (1*E*,3*E*,5*E*)-1,3,4,6-Tetraarylhexa-1,3,5-trienes

Preparation of **1a**–**1f** was effected by diphosphorylation of (*E*)-1,4-dibromo-2,3-diphenylbut-2-ene (**2**)[9] with triethylphosphite followed by two-fold Horner–Wadsworth–Emmons reaction with *p*-substituted benzaldehydes (Scheme 1).[10] Trienes **1** were isolated in moderate to high yields as a single stereoisomer by silica gel column chromatography followed by recrystallization in all cases.



Scheme 1. Synthesis of (1*E*,3*E*,5*E*)-1,6-diaryl-3,4-diphenylhexa-1,3,5-trienes **1a**–**1f**. Reagents and conditions: a) $P(OEt)_3$, 150 °C; b) for **1a**, C_6H_5CHO, NaH, THF, 50 °C; for **1b**, 4-CF_3-C_6H_4CHO, *t*BuOK, DMF, 50 °C; for **1c**, 4-Cl-C_6H_4CHO, NaH, DMF, 50 °C; for **1d**, 4-MeO-C_6H_4CHO, NaH, 15-crown-5, DMF, 50 °C; for **1e**, 4-CN-C_6H_4CHO, NaH, THF, reflux; for **1f**, 4-C_6H_5-C_6H_4CHO, NaH, DMF, 50 °C.

Trienes **1g**–**1j** were synthesized starting from an *E*/*Z* (9:91) mixture of 2,3-bis(4-bromophenyl)but-2-ene (**4**)[11] as shown in Scheme 2. Thus, dibromination of **4** with *N*-bromosuccinimide in the presence of dibenzoyl peroxide in CCl_4,[12] proceeded with isomerization of the olefin geometry to give an *E*/*Z* (80:20) mixture of tetrabromide **5** which was transformed into 3,4-bis(4-bromophenyl)-1,6-bis(4-trifluoromethylphenyl)hexa-1,3,5-triene (**7**) as a mixture of (1*E*,3*E*,5*E*)- and (1*E*,3*Z*,5*E*)-isomers (73:27), in a manner similar to the preparation of **1b**.[13] Stereochemically pure (1*E*,3*E*,5*E*)-**7**, isolated from the mixture by recrystallization, was subjected to Pd-catalyzed amination with piperidine or Ph_2NH,[14] and hydroxylation with KOH[15] followed by alkylation with methyl or isopropyl iodide according to the protocols developed by Buchwald and co-workers, giving rise to (1*E*,3*E*,5*E*)-trienes **1g**–**1j**, respectively (Scheme 2).



Scheme 2. Synthesis of (1*E*,3*E*,5*E*)-3,4-diaryl-1,6-bis(4-trifluoromethylphenyl)hexa-1,3,5-trienes **1g**–**1j**. Reagents and conditions: a) *N*-bromosuccinimide, dibenzoyl peroxide, CCl_4, reflux; b) $P(OEt)_3$, 120 °C; c) 4-CF_3-C_6H_4CHO, NaOMe, DMF, 50 °C; d) for **1g**, piperidine, Pd(tBu$_3$P)$_2$ (5 mol %), NaO*t*Bu (3 equiv), toluene, 100 °C; for **1h**, diphenylamine, Pd(tBu$_3$P)$_2$ (5 mol %), NaO*t*Bu (3 equiv), toluene, 100 °C; e) KOH, Pd_2dba_3 (2 mol %), 2-di(*tert*-butyl)phosphino-2′,4′,6′-triisopropylbiphenyl, hexane/H_2O, 100 °C; f) for **1i**, MeI, K_2CO_3, acetone, 60 °C; for **1j** *i*PrI, K_2CO_3, Bu_4NI, acetone, 60 °C.

Abstract in Japanese:

パラ置換ベンズアルデヒド２分子と(E)-2,3-ジアリール-1,4-ビス（ジエチルホスホニル）-2-ブテンとの Horner–Wadsworth–Emmons 反応により、(1E,3E,5E)-1,3,4,6-テトラアリール-1,3,5-ヘキサトリエンを中程度ないし良好な収率で合成した。1,6 位のフェニル基のパラ位に電子求引基や電子供与基を置換すると、紫外吸収スペクトルは母体の 1,3,4,6-テトラフェニル-1,3,5-ヘキサトリエンよりも長波長シフトした。これらのトリエンはクロロホルム溶液中では蛍光を示さないのに対し、粉末状態では量子収率 0.15~0.44 で蛍光発光することを明らかにした。3,4-位のフェニルのパラ位にアミノ基を導入すると、蛍光発光極大が赤色移動した。単結晶X線構造解析により 1,3,4,6-テトラフェニル-1,3,5-ヘキサトリエンのトリエン部位は完全な平面構造をしていること、3,4 位のフェニル基はいずれもトリエン平面に対して 82°振れて配置していることがわかった。隣接する分子どうしは 9.3Å 以上離れており、その結果蛍光の消光につながる分子間相互作用が妨げられていると考えている。

UV and Fluorescence Spectra

Absorption spectra of **1a**–**1f** measured in $CHCl_3$ are shown in Figure 2 and photophysical properties of **1** are summarized in Table 1. All spectra of **1a**–**1f** showed almost identi-

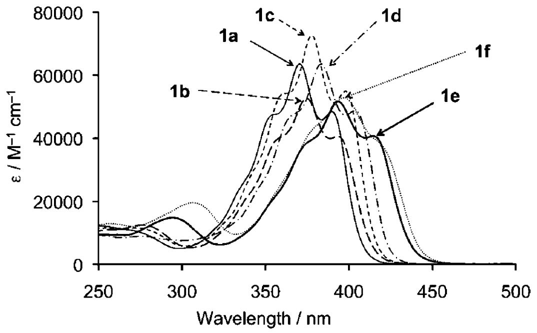


Figure 2. UV absorption spectra of **1a**–**1f** measured in $CHCl_3$.

Table 1. Photophysical properties of **1**.

Compd	Absorption[a] λ_{max} [nm][c]	ε [$M^{-1}cm^{-1}$]	Fluorescence[b] λ_{max} [nm][d]	Φ_f[e]
1a	370	63600	459	0.25
1b	375	52700	509	0.40
1c	378	72500	464	0.30
1d	383	63500	497	0.22
1e	393	51700	513	0.26
1f	397	52900	525	0.33
1g	373	37000	551	0.44
1h	312	50400	549	0.15
1i	378	47800	488	0.43
1j	379	41700	491	0.26

[a] Measured in $CHCl_3$. [b] Excitation of **1** in powder form was effected with UV light ($\lambda = 365$ nm). [c] Wavelength of absorption maxima with the largest molar extinction coefficient. [d] Wavelength of emission maxima. [e] Absolute quantum yield determined by a calibrated integrating sphere system.

cal vibrational structures, which were similar to that of (1*E*,3*E*,5*E*)-1,6-diphenylhexa-1,3,5-triene.[8] The absorption maxima in $CHCl_3$ slightly red-shifted compared with those of the corresponding 3,4-unsubstituted counterparts depending on the *p*-substituents of the terminal phenyl groups.

Although solutions of **1a–1f** in $CHCl_3$ did not exhibit detectable fluorescence upon irradiation with UV light, solid **1a–1f** emitted blue or green light with solid-state quantum yields ranging from 0.22 to 0.40 (Figure 3 and Table 1). Thus, **1a–1f** are AIE-active. No fluorescence of **1a–1f** in solutions may be ascribed to intramolecular rotation of multiple phenyl groups in solutions, which results in consumption of all the photon energies and deactivation of all the excited states in solutions. This observation is in marked contrast to the fluorescence behavior of (1*E*,3*E*,5*E*)-1,6-bis(*p*-substituted phenyl)hexa-1,3,5-trienes that are efficiently emissive in solution with good to high quantum yields but nearly nonemissive in microcrystalline state presumably arising from the close packing of the planar skeletons in the aggregates.[8] Therefore, the 3,4-diphenyl groups whose rotation is limited in the solid state appear to suppress intermolecular interactions in the aggregates, which is responsible for the quenching of emission (for molecular and crystal structures of **1a**, see below).

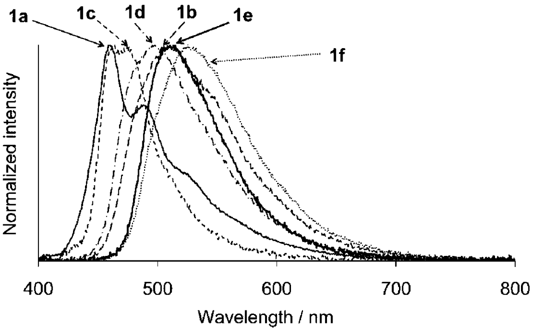


Figure 3. Fluorescence spectra of **1a–1f** in powder form.

Since the solid-state quantum yield of **1b** was the highest, we further investigated the photophysical properties of **1g–1i** bearing CF_3 groups at the molecular termini. The absorption in $CHCl_3$ and solid-state fluorescence spectra of **1g–1i** are shown in Figures 4 and 5, respectively, together with those of **1b**. Alkoxy-substituted **1i** and **1j** showed absorption spectra similar to that of **1b**, whereas the absorption edges of the amino derivatives **1g** and **1h** were significantly red-shifted relative to those of **1b**, **1i**, and **1j**. Thus, the introduction of amino groups at the *para* position of the 3,4-diphenyl groups largely affected the electronic structure to result in the decrease in the HOMO–LUMO gap (see MO Calculation section). Emission maxima of **1g** and **1h** were bathochromically shifted, whereas those of **1i** and **1j** were blue-shifted compared with **1b**. The quantum yields of **1g** and **1i** were almost the same as that of **1b**, but much higher than those of **1h** and **1j**, respectively. Therefore, the incorporation of piperidyl and methoxy groups can lead to fine tuning of emission colors, maintaining the good efficiency of the solid-state emission.

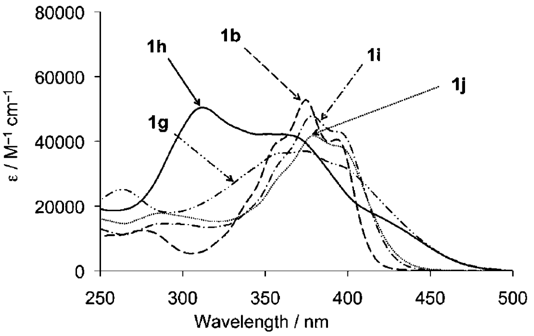


Figure 4. UV absorption spectra of **1b** and **1g–1j** measured in $CHCl_3$.

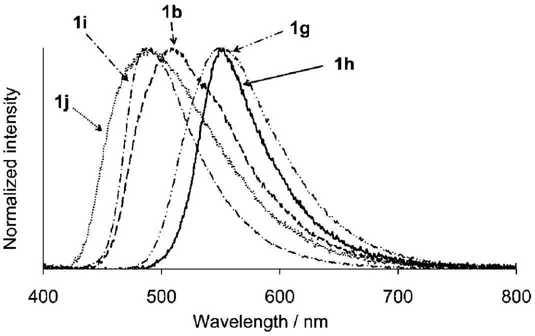


Figure 5. Fluorescence spectra of **1b** and **1g–1j** in powder form.

Fluorescence spectra of **1g** in a mixed solvent of CH_3CN and water were also measured (Figure 6). A CH_3CN solution of **1g** was nonluminescent, whereas the fluorescence intensity remarkably increased when **1g** was dissolved in the mixtures of CH_3CN and water. The highest intensity was observed with the water content of 70 vol% and further addition of water resulted in a decrease in fluorescence intensity. As water was a poor solvent for **1g**, dilution with water should have induced aggregation of **1g**. Thus, aggregation-induced emission was again confirmed.

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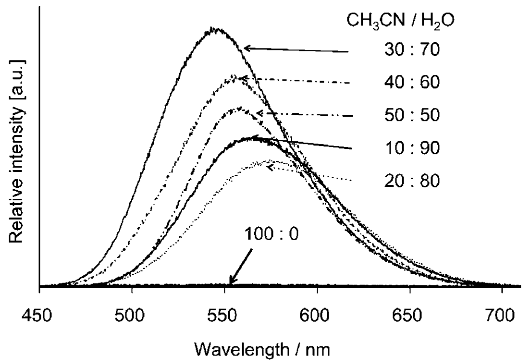

Figure 6. Fluorescence spectra of **1g** in a mixture of CH_3CN and H_2O.

Molecular and Crystal Structures

Single crystals of **1a** were obtained by recrystallization from a hexane solution. X-ray structural analysis of a single crystal reveals that the triene crystallizes in the monoclinic space group $P2_1/c$ [cell parameters: $a = 10.2356(17)$, $b = 9.3494(15)$, $c = 11.6070(18)$, $\beta = 91.244(3)$] with $Z = 2$.[16] The triene moiety of **1a** was found to adapt a completely planar conformation (Figure 7a), whereas the terminal benzene rings were slightly distorted with dihedral angles of 15° (Figure 7b). The remaining 3,4-diphenyl groups oriented almost perpendicular (82°) to the plane of the triene moiety (Figure 7a). Crystal packing of **1a**, shown in Figure 8, reveals that each molecule located at the edges of the unit cell was well-separated from one another, and the triene plane was crossed (not in parallel) with that of the molecule positioned at the center of the cell.[17] Thus, the tight packing leading to fluorescence quenching is well-prevented owing probably to the presence of the 3,4-diphenyl groups.

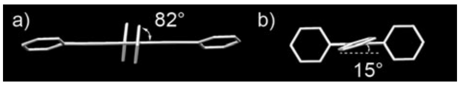

Figure 7. Illustration of molecular structure of **1a** in the crystal (hydrogens are omitted for clarity): a) side view of the molecule; b) view from long axis of the molecule.

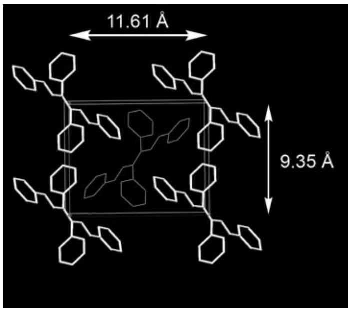

Figure 8. Packing diagram of **1a** (hydrogens are omitted for clarity).

MO Calculation

Molecular orbital calculations of **1a**, **1b**, **1i**, and dimethylamino analog **1g′**, a model compound of **1g**, were carried out by the DFT method at the B3LYP/6-31G*//B3LYP/6-31G* level using the Gaussian 03 package.[18] The results are summarized in Table 2 and the HOMO and LUMO drawings are shown in Figure 9. For **1a** and **1b**, both the HOMOs and LUMOs were localized over the Ph-triene-Ph skeleton and not developed on the 3,4-diphenyl groups. Compared with **1a** and **1b**, the introduction of trifluoromethyl groups at the

Table 2. HOMO and LUMO energies of **1a**, **1b**, **1i**, and **1g′**.[a]

Compound	**1a**	**1b**	**1i**	**1g′**
LUMO [eV]	−1.79	−2.32	−2.21	−2.02
HOMO [eV]	−4.95	−5.37	−5.18	−4.79
HOMO–LUMO gap [eV] (calculated)	3.16	3.05	2.97	2.77
HOMO–LUMO gap [eV] (experimental)[b]	2.89	2.72	2.75	2.50[c]

[a] Calculated at the B3LYP/6–31G*//B3LYP/6–31G* level. [b] Energy gaps were estimated from the absorption edges of UV/Vis absorption spectra. [c] The value of **1g**.

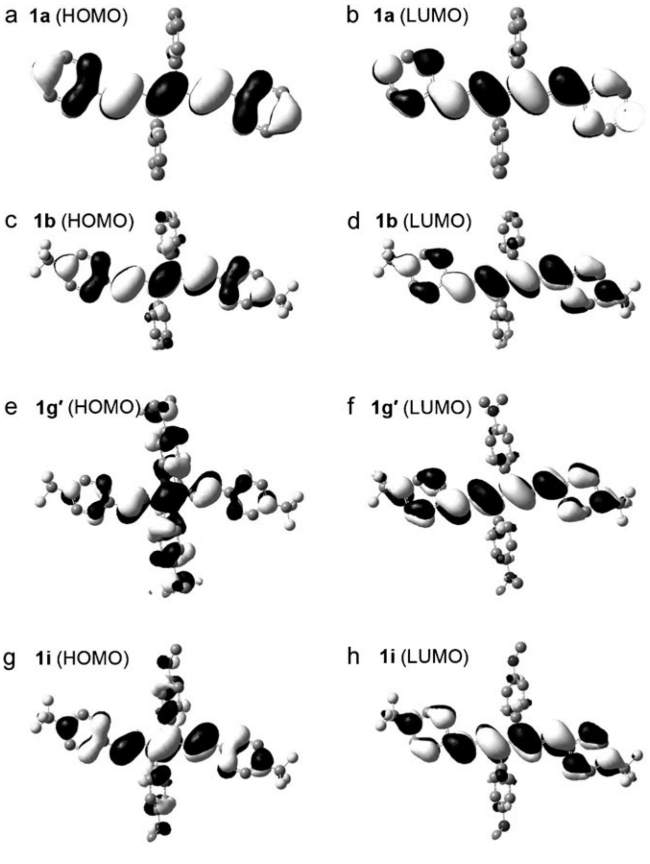

Figure 9. Molecular orbital drawings of the HOMOs and LUMOs of **1a**, **1b**, **1i**, and **1g′**.

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terminal phenyl groups lowered both the HOMOs and LUMOs, and resulted in a decrease in the HOMO–LUMO gap. Meanwhile, substitution of a methoxy group at the *para* position of both 3,4-diphenyl groups of **1b** resulted in a slight extension of the HOMO over the methoxy-substituted phenyl groups (**1i**). In case of dimethylamino derivative **1g′**, HOMO was extensively developed over not only the 1,6-diphenylhex-1,3,5-triene skeleton but also the stilbene moiety (Figure 9, left of the bottom), and the energy level was raised greatly. On the other hand, LUMO of **1g′** was found to localize over only the long axis of the molecular skeleton as similar to the other trienes. The longer emission maxima of **1g** and **1h** may be ascribed to the amino group-induced change of the electronic structures. The trend of the HOMO–LUMO energy gaps is consistent with the absorption edges in the UV/Visible spectra shown in Figures 2 and 4.

Conclusions

In summary, we have demonstrated that (1*E*,3*E*,5*E*)-1,3,4,6-tetraarylhexa-1,3,5-trienes are a new class of chromophores that exhibit aggregation-induced emission. The fluorescence color of the trienes in the solid state can be tuned from blue to green by substituting functional groups such as alkoxy, amino, chloro, cyano, phenyl, and trifluoromethyl groups at the *para* position of the phenyl groups. Moreover, the introduction of trifluoromethyl groups at the molecular termini induced good quantum yields of solid-state fluorescence ($\Phi_f = 0.40$–0.44). Our ongoing research is directed toward development of highly fluorescent organic solids based on the molecular design of the present study.

Experimental Section

General

Melting points were determined using a Yanagimoto Micro Point Apparatus. ^{1}H NMR spectra were measured on Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane ($\delta = 0$ ppm) or chloroform ($\delta = 7.26$ ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{13}C NMR spectra were measured on Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with tetramethylsilane ($\delta = 0$ ppm) or chloroform ($\delta = 77.0$ ppm) as an internal standard. ^{19}F NMR spectra were measured on a Varian Mercury 300 (282 MHz) spectrometer with $CFCl_3$ as an internal standard ($\delta = 0$ ppm). Chemical shift values are given in parts per million downfield relative to the internal standards. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. EI-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. FAB-MS analyses were performed with a JEOL-HX110A spectrometer. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at the Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F254, and column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Gel permeation chromatography (GPC) was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using JAIGEL-1H and -2H columns. Reagent-grade dichloromethane, diethyl ether, and tetrahydrofuran were passed through two packed columns of neutral alumina and copper oxide, respectively, under a nitrogen atmosphere before use. All reactions were carried out under an argon atmosphere. UV absorption spectra were recorded with a Shimadzu UV-2100PC spectrometer. Fluorescence spectra and absolute quantum yields were recorded with a Hamamatsu Photonics C9920–02 Absolute PL Quantum Yield Measurement System.

Synthesis

(*E*)-1,4-Bis(diethylphosphonyl)-2,3-diphenylbut-2-ene (3): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **2** (2.2 g, 6.7 mmol) and triethylphosphite (4.7 mL, 27 mmol) at room temperature. The mixture was heated at 150 °C for 12 h. After cooling to room temperature, the resulting mixture was dissolved in hexane, cooled at 0 °C. The precipitates were filtered through a glass filter and washed with cold hexane. The product was purified by recrystallization from hexane to give **3** (2.1 g, 65 %) as a colorless solid. $R_f = 0.24$ (ethyl acetate); m.p.: 86.5–87.7 °C; IR (KBr): $\tilde{\nu} = 3518$, 3458, 2984, 2907, 1645, 1601, 1493, 1443, 1391, 1367, 1238, 1165, 1097, 1028, 966, 891, 779, 708, 660, 554, 521 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.07$ (t, $J = 7.2$ Hz, 12 H), 2.91 (d, $J = 18.4$ Hz, 4 H), 3.62–3.85 (m, 8 H), 7.27–7.31 (m, 2 H), 7.36–7.44 ppm (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.3$, 34.0 (dd, $J = 141.1$, 6.1 Hz), 61.4, 127.1, 128.1, 129.0, 132.4, 140.4 ppm; MS (FAB): *m*/*z* (%): 482 (26) $[M+2]^+$, 481 (100) $[M+1]^+$, 480 (15) M^+; MS (FAB-HR): *m*/*z* (%) calcd for $C_{24}H_{34}O_6P_2$: 480.1831; found: 480.1821.

(1*E*,3*E*,5*E*)-1,3,4,6-Tetraphenylhexa-1,3,5-triene (1a): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **3** (48 mg, 0.10 mmol), NaH (9.4 mg, 0.39 mmol), and THF (4 mL). To the solution was added benzaldehyde (21 µL, 0.21 mmol) at room temperature. The resulting solution was stirred at 50 °C for 69 h before quenching with water (5 mL). The aqueous layer was extracted with diethyl ether (5 mL × 3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was washed with methanol to give **1a** (33 mg, 87 %) as a pale yellow solid. $R_f = 0.63$ (hexane/ethyl acetate 10:1); m.p.: 173.1 °C; IR (KBr): $\tilde{\nu} = 3030$, 1595, 1574, 1489, 1442, 1315, 1146, 1070, 1024, 961, 908, 750, 704, 689, 577, 556, 525 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.07$ (d, $J = 16.0$ Hz, 2 H), 6.92 (d, $J = 16.0$ Hz, 2 H), 7.10–7.53 ppm (m, 20 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 126.5$, 127.3, 127.4, 128.3, 128.5, 130.4, 130.8, 132.4, 137.6, 138.9, 141.0 ppm; MS (EI): *m*/*z* (%): 386 (7) $[M+2]^+$, 385 (31) $[M+1]^+$, 384 (100) M^+; elemental analysis: calcd (%) for $C_{30}H_{24}$: C 93.71, H 6.29; found: C 93.72, H 6.53.

(1*E*,3*E*,5*E*)-3,4-Diphenyl-1,6-bis[4-(trifluoromethyl)phenyl]hexa-1,3,5-triene (1b): An oven-dried Schlenk tube (80 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **3** (96 mg, 0.20 mmol), *t*BuOK (88 mg, 0.78 mmol), and DMF (16 mL). To the solution was added 4-(trifluoromethyl)benzaldehyde (57 µL, 0.42 mmol) at room temperature. The resulting solution was stirred at 50 °C for 22 h before quenching with water (10 mL). The aqueous layer was extracted with diethyl ether (5 mL × 3). The combined organic layer was washed with saturated aqueous NaCl (10 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 5:1) followed by recrystallization from hexane-dichloromethane to give **1b** (56 mg, 54 %) as a pale yellow solid. $R_f = 0.61$ (hexane/ethyl acetate 5:1); m.p.: 204.3–204.9 °C; IR (KBr): $\tilde{\nu} = 3051$, 2930, 1609, 1491, 1443, 1414, 1327, 1286, 1188, 1161, 1153, 1119, 1067, 1015, 962, 951, 868, 822, 766, 702, 675, 600, 453 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.12$ (d, $J = 16.0$ Hz, 2 H), 6.98 (d, $J = 16.0$ Hz, 2 H), 7.17 (AA′BB′, 4 H), 7.36–7.38 (m, 4 H), 7.43 (AA′BB′, 4 H), 7.46–7.50 (m, 2 H), 7.51–7.55 ppm (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 124.0$ (q, $J = 269.1$ Hz), 125.3 (q, $J = 3.8$ Hz), 126.4, 127.7, 128.3, 128.9 (q, $J = 32.0$ Hz), 130.5, 131.4, 132.3, 138.1, 140.7, 141.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -63.1$ ppm; MS (FAB): *m*/*z* (%): 522 (9) $[M+2]^+$, 521 (41) $[M+1]^+$, 520 (100) M^+; elemental analysis: calcd (%) for $C_{32}H_{22}F_6$: C 73.84, H 4.26; found: C 73.86, H 4.49.

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(1*E*,3*E*,5*E*)-1,6-Bis(4-chlorophenyl)-3,4-diphenylhexa-1,3,5-triene (1c): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **3** (48 mg, 0.10 mmol), NaH (9.4 mg, 0.39 mmol), and DMF (7 mL). To the solution was added a solution of 4-chlorobenzaldehyde (30 mg, 0.21 mmol) in DMF (1 mL) at room temperature. The resulting solution was stirred at 50 °C for 45 h before quenching with water (5 mL). The aqueous layer was extracted with diethyl ether (5 mL×3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 5:1) followed by recrystallization from toluene to give **1c** (26 mg, 48 %) as a pale yellow solid. $R_f = 0.61$ (hexane/ethyl acetate 5:1); m.p.: 208.9–209.2 °C; IR (KBr): $\tilde{\nu} = 3038$, 1489, 1443, 1321, 1292, 962, 862, 764, 704, 615, 490, 473 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.01$ (d, $J = 16.0$ Hz, 2H), 6.86 (d, $J = 16.0$ Hz, 2H), 7.00 (AA′BB′, 2H), 7.14 (AA′BB′, 2H), 7.33–7.36 (m, 4H), 7.43–7.47 (m, 2H), 7.49–7.53 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 127.4$, 127.5, 128.2, 128.5, 130.56, 130.64, 131.2, 132.8, 135.9, 138.5, 141.1 ppm; MS (FAB): *m/z* (%): 456 (15) $[M+4]^+$, 455 (26) $[M+3]^+$, 454 (72) $[M+2]^+$, 453 (39) $[M+1]^+$, 452 (100) M^+; HRMS: *m/z* (%) calcd for $C_{30}H_{22}Cl_2$: 452.1099; found: 452.1087.

(1*E*,3*E*,5*E*)-1,6-Bis(4-methoxyphenyl)-3,4-diphenylhexa-1,3,5-triene (1d): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **3** (48 mg, 0.10 mmol), NaH (9.4 mg, 0.39 mmol), 15-crown-5 (44 mg, 0.20 mmol), and DMF (5 mL). To the solution was added 4-anisaldehyde (25 μL, 0.21 mmol) at room temperature. The resulting solution was stirred at 50 °C for 74 h before quenching with water (5 mL). The aqueous layer was extracted with diethyl ether (5 mL×3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 5:1) followed by recrystallization from ethanol to give **1d** (37 mg, 86 %) as a pale yellow solid. $R_f = 0.42$ (hexane/ethyl acetate 5:1); m.p.: 189.3–189.8 °C; IR (KBr): $\tilde{\nu} = 2999$, 2831, 1603, 1570, 1508, 1458, 1441, 1420, 1302, 1288, 1246, 1173, 1030, 961, 922, 858, 818, 758, 700, 642, 565, 519 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.75$ (s, 6H), 5.99 (d, $J = 15.6$ Hz, 2H), 6.70–6.73 (m, 4H), 6.78 (d, $J = 15.6$ Hz, 2H), 7.01–7.04 (m, 4H), 7.35–7.37 (m, 4H), 7.41–7.45 (m, 2H), 7.49–7.52 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.3$, 113.8, 127.0, 127.5, 128.1, 128.4, 130.5, 130.7, 131.3, 139.1, 140.1, 158.8 ppm; MS (FAB): *m/z* (%): 446 (14) $[M+2]^+$, 445 (37) $[M+1]^+$; HRMS (FAB): *m/z* (%) calcd for $C_{32}H_{28}O_2$: 444.2089; found: 444.2080.

(1*E*,3*E*,5*E*)-1,6-Bis(4-cyanophenyl)-3,4-diphenylhexa-1,3,5-triene (1e): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **3** (48 mg, 0.10 mmol), NaH (9.4 mg, 0.39 mmol), and THF (6 mL). To the solution was added a solution of 4-formylbenzonitrile (28 mg, 0.21 mmol) in DMF (2 mL) at room temperature. The resulting solution was refluxed for 12 h. The mixture was quenched with water (5 mL). The aqueous layer was extracted with diethyl ether (5 mL×3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was washed with methanol and the residue was recrystallized from benzene to give **1e** (26 mg, 59 %) as a yellow solid. $R_f = 0.32$ (hexane/ethyl acetate 5:1); m.p.: 214.4–215.1 °C; IR (KBr): $\tilde{\nu} = 3032$, 2222, 1597, 1504, 1493, 1443, 1410, 1329, 1288, 1173, 961, 943, 928, 866, 852, 814, 768, 708, 670, 631, 563, 532, 494, 419 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.09$ (d, $J = 16.0$ Hz, 2H), 7.00 (d, $J = 15.6$ Hz, 2H), 7.15 (AA′BB′, 4H), 7.34–7.36 (m, 4H), 7.45 (AA′BB′, 4H), 7.49–7.56 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 110.2$, 118.9, 126.7, 127.9, 128.38, 128.42, 130.4, 131.4, 132.1, 133.2, 137.7, 141.6, 142.3 ppm; MS (FAB): *m/z* (%): 436 (26) $[M+2]^+$, 435 (81) $[M+1]^+$, 434 (100) M^+; HRMS (FAB): *m/z* (%) calcd for $C_{32}H_{22}N_2$: 434.1783; found: 434.1802.

(1*E*,3*E*,5*E*)-1,6-Bis(4-biphenylyl)-3,4-diphenylhexa-1,3,5-triene (1f): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **3** (48 mg, 0.10 mmol), NaH (9.4 mg, 0.39 mmol), and DMF (10 mL). To the solution was added a solution of 4-phenylbenzaldehyde (38 mg, 0.21 mmol) in DMF (2 mL) at room temperature. The resulting solution was stirred at 50 °C for 15 h before quenching with water (10 mL). The aqueous layer was extracted with diethyl ether (5 mL×3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was purified by recrystallization from chloroform to give **1f** (35 mg, 65 %) as a yellow solid. $R_f = 0.55$ (hexane/ethyl acetate 5:1); m.p.: 229.0–229.2 °C; IR (KBr): $\tilde{\nu} = 3026$, 1599, 1487, 1443, 1408, 1317, 1279, 1074, 1024, 1005, 964, 866, 824, 760, 698, 675, 654, 637, 586, 563, 421 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.12$ (d, $J = 16.0$ Hz, 2H), 7.98 (d, $J = 16.0$ Hz, 2H), 7.17 (AA′BB′, 4H), 7.29–7.33 (m, 2H), 7.38–7.42 (m, 8H), 7.44 (AA′BB′, 4H), 7.46–7.49 (m, 2H), 7.51–7.55 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 126.7$, 126.8, 127.0, 127.1, 127.3, 128.2, 128.6, 130.4, 130.7, 131.9, 136.6, 138.8, 139.8, 140.4, 141.0 ppm; MS (FAB): *m/z* (%): 537 (8) $[M+1]^+$, 536 (15) M^+; HRMS (FAB): *m/z* (%) calcd for $C_{42}H_{32}$: 536.2504; found: 536.2495.

(*E*)-1,4-Dibromo-2,3-bis(4-bromophenyl)-but-2-ene (5): An oven-dried Schlenk tube (250 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **4** (2.7 g, 7.2 mmol), *N*-bromosuccinimide (2.8 g, 16 mmol), benzoyl peroxide (174 mg, 0.72 mmol), and carbon tetrachloride (72 mL) at room temperature. The resulting solution was refluxed for 3 h. After cooling to room temperature, the solution was added with saturated aqueous sodium thiosulfate (100 mL) and dichloromethane (50 mL). The aqueous layer was extracted with dichloromethane (5 mL×3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The product was purified by recrystallization from hexane to give **5** (2.6 g, 68 %) as an 80:20 mixture of (*E*)- and (*Z*)-isomers as a colorless solid. Mixture: $R_f = 0.30$ (hexane/dichloromethane 10:1); m.p.: 197.7–198.7 °C; IR (KBr): $\tilde{\nu} = 1587$, 1487, 1435, 1395, 1209, 1074, 1011, 922, 829, 743, 619, 540 cm^{-1}; (*E*)-isomer: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.98$ (s, 4H), 7.33 (AA′BB′, 4H), 7.60 ppm (AA′BB′, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 34.9$, 122.5, 129.8, 131.8, 136.5, 138.4 ppm; (*Z*)-isomer: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.44$ (s, 4H), 6.94 (AA′BB′, 4H), 7.31 ppm (AA′BB′, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 31.7$, 121.8, 130.6, 131.3, 137.8, 139.1 ppm; MS (EI): *m/z* (%): 528 (2) $[M+8]^+$, 526 (9) $[M+6]^+$, 524 (12) $[M+4]^+$, 522 (9) $[M+2]^+$, 443 (7) $[M-77]^+$, 366 (41) $[M-154]^+$, 364 (87) $[M-156]^+$, 362 (58) $[M-158]^+$, 284 (59) $[M-236]^+$, 282 (56) $[M-238]^+$, 204 (100) $[M-316]^+$; elemental analysis: calcd (%) for $C_{16}H_{12}Br_4$: C 36.68, H 2.31; found: C 36.54, H 2.56.

(*E*)-2,3-Bis(4-bromophenyl)-1,4-bis(diethylphosphonyl)-2-butene (6): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **5** (2.3 g, 4.3 mmol), and triethylphosphite (2.6 mL, 15 mmol) at room temperature. The resulting mixture was heated at 120 °C for 23 h. After cooling to room temperature, the solution was added with hexane. Cooling the solution to 0 °C gave precipitates, which were filtered and washed with hexane to afford **6** (1.6 g, 58 %) as a colorless solid. $R_f = 0.43$ (ethyl acetate); m.p.: 111.3–112.3 °C; IR (KBr): $\tilde{\nu} = 3447$, 2980, 1489, 1391, 1246, 1161, 1063, 1045, 1024, 968, 951, 826, 791, 767, 600, 550, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.12$ (t, $J = 7.2$ Hz, 12H), 2.82 (d, $J = 18.4$ Hz, 4H), 3.73–3.88 (m, 8H), 7.30–7.33 (m, 4H), 7.51–7.53 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.3$ (t, $J = 3.1$ Hz), 34.1 (dd, $J = 141.8$, 6.1 Hz), 61.6 (t, $J = 3.0$ Hz), 121.4, 131.3, 132.0, 139.1 ppm; MS (FAB): *m/z* (%): 641 (53) $[M+5]^+$, 639 (100) $[M+3]^+$, 637 (52) $[M+1]^+$; HRMS: *m/z* (%) calcd for $C_{24}H_{32}Br_2O_6P_2$: 637.0119; found: 637.0137.

(1*E*,3*E*,5*E*)-3,4-Bis(4-bromophenyl)-1,6-bis[4-(trifluoromethyl)phenyl]-hexa-1,3,5-triene (7): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **6** (0.64 g, 1.0 mmol), NaOMe (0.12 g, 2.2 mmol), and DMF (10 mL). To the solution was added 4-trifluoromethylbenzaldehyde (0.30 mL, 2.2 mmol) at room temperature. The resulting mixture was stirred at 50 °C for 6 h before quenching with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with dichloromethane (5 mL×3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was washed with methanol to afford **7** (0.58 g, 86 %) in a 73:27 mixture of (1*E*,3*E*,5*E*)- and (1*E*,3*Z*,5*E*)-isomers as a yellow solid. Stereochemically pure (1*E*,3*E*,5*E*)-**7** was obtained by recrystallization from chloroform. (1*E*,3*E*,5*E*)-isomer: $R_f = 0.22$ (hexane/dichloromethane 10:1); m.p.: 207.5–208.4 °C; IR (KBr): $\tilde{\nu} = 3044$, 1609, 1487, 1325, 1163, 1117, 1067, 1013, 968, 870, 824, 596, 467 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.10$ (d, $J = 16.0$ Hz, 2 H), 6.91 (d, $J = 16.0$ Hz, 2 H), 7.20–7.25 (m, 8 H), 7.47 (AA′BB′, 4 H), 7.65–7.68 ppm (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 122.0$, 123.9 (q, $J = 269.9$ Hz), 125.4 (q, $J = 3.8$ Hz), 126.6, 129.3 (q, $J = 32.8$ Hz), 131.1, 131.4, 131.7, 132.2, 136.8, 140.3, 140.6 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -63.1$ ppm; MS (FAB): m/z (%): 680 (57) $[M+4]^+$, 678 (100) $[M+2]^+$, 676 (58) M^+; elemental analysis: calcd (%) for $C_{32}H_{20}Br_2F_6$: C 56.66, H 2.97; found: C 56.43, H 2.99.

(1*E*,3*E*,5*E*)-3,4-Bis(4-piperidinophenyl)-1,6-bis[4-(trifluoromethyl)phenyl]hexa-1,3,5-triene (1g): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **7** (68 mg, 0.10 mmol), piperidine (24 µL, 0.24 mmol), Pd ($PtBu_3$)$_2$ (5 µmol, 3 mg), NaO*t*Bu (29 mg, 0.30 mmol), and toluene (2 mL) at room temperature. The resulting solution was stirred at 100 °C for 22 h before quenching with saturated aqueous NH_4Cl (2 mL). The aqueous layer was extracted with dichloromethane (5 mL × 3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was washed with hot ethanol and the residue was recrystallized from hexane/toluene (1:1) to give **1g** (46 mg, 67 %) as a yellow solid. $R_f = 0.50$ (hexane/dichloromethane 1:1); m.p.: 218.0–219.5 °C; IR (KBr): $\tilde{\nu} = 2938$, 1607, 1514, 1452, 1416, 1385, 1323, 1234, 1165, 1125, 1067, 968, 872, 826 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.66$ (m, 4 H), 1.80 (m, 8 H), 3.30 (t, $J = 5.4$ Hz, 8 H), 6.21 (d, $J = 16.0$ Hz, 2 H), 7.04 (AA′BB′, 4 H), 7.10 (d, $J = 16.0$ Hz, 2 H), 7.20–7.24 (m, 8 H), 7.43 ppm (AA′BB′, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 24.4$, 26.1, 50.3, 115.6, 124.1 (q, $J = 269.2$ Hz), 125.2 (d, $J = 3.8$ Hz), 126.4, 128.5 (q, $J = 32.1$ Hz), 128.8, 130.6, 131.6, 133.4, 141.2, 141.6, 151.2 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -62.9$ ppm; MS (FAB): m/z (%): 688 (23) $[M+2]^+$, 687 (70) $[M+1]^+$, 686 (100) M^+; elemental analysis: calcd (%) for $C_{42}H_{40}F_6N_2$: C 73.45, H 5.87; found: C 73.53, H 5.81.

(1*E*,3*E*,5*E*)-3,4-Bis[4-(*N*,*N*-diphenylamino)phenyl]-1,6-bis[4-(trifluoromethyl)phenyl]hexa-1,3,5-triene (1h): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **7** (68 mg, 0.10 mmol), diphenylamine (37 mg, 0.22 mmol), Pd ($PtBu_3$)$_2$ (3 mg, 5 µmol), NaO*t*Bu (29 mg, 0.30 mmol), and toluene (1.4 mL) at room temperature. The resulting solution was stirred at 100 °C for 21 h before quenching with saturated aqueous NH_4Cl (2 mL). The aqueous layer was extracted with dichloromethane (5 mL × 3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was passed through a short pad of florisil (eluent: dichloromethane) and the organic solvent was removed under reduced pressure. The residue was purified by GPC (eluent: chloroform) followed by recrystallization from hexane-toluene (1:1) to give **1h** (46 mg, 54 %) as a yellow solid. $R_f = 0.23$ (hexane/dichloromethane 5:1); m.p.: 198.8–199.8 °C; IR (KBr): $\tilde{\nu} = 3038$, 1609, 1591, 1508, 1491, 1323, 1283, 1165, 1111, 1065, 826, 758, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.30$ (d, $J = 16.0$ Hz, 2 H), 7.07–7.12 (m, 6 H), 7.20–7.25 (m, 16 H), 7.27–7.34 (m, 12 H), 7.50 ppm (AA′BB′, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 122.6$, 123.2, 125.4 (q, $J = 269.6$ Hz), 124.6, 125.3 (q, $J = 3.8$ Hz), 126.4, 128.8 (q, $J = 32.4$ Hz), 129.3, 131.0, 131.5, 131.8, 132.8, 141.0, 141.5, 147.2, 147.4 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -63.0$ ppm; MS (FAB): m/z (%): 856 (39) $[M+2]^+$, 855 (88) $[M+1]^+$, 854 (100) M^+; elemental analysis: calcd (%) for $C_{56}H_{40}F_6N_2$: C 78.67, H 4.72; found: C 78.59, H 4.88.

(1*E*,3*E*,5*E*)-3,4-Bis(4-hydroxyphenyl)-1,6-bis[4-(trifluoromethyl)phenyl]hexa-1,3,5-triene (8): An oven-dried Schlenk tube (20 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **7** (0.25 g, 0.37 mmol), KOH (0.13 g, 2.2 mmol), $Pd_2(dba)_3$ (17 mg, 0.020 mmol), 2-di(*t*-butyl)phosphino-2′,4′,6′-triisopropylbiphenyl (16 mg, 0.040 mmol), water (0.22 mL), and dioxane (2 mL) at room temperature. The solution was heated at 100 °C for 20 h before quenching with saturated aqueous NH_4Cl (4 mL). The aqueous layer was extracted with dichloromethane (5 mL × 3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was purified by column chromatography on silica gel (dichloromethane) to give **8** (0.19 g, 95 %) as a yellow solid. $R_f = 0.21$ (dichloromethane); m.p.: 224.0–225.2 °C; IR (KBr): $\tilde{\nu} = 3360$, 1611, 1508, 1456, 1327, 1244, 1165, 1111, 1067, 968, 837, 419 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.85$ (s, 2 H), 6.16 (d, $J = 16.0$ Hz, 2 H), 6.98 (AA′BB′, 4 H), 7.02 (d, $J = 16.0$ Hz, 2 H), 7.20–7.23 (m, 8 H), 7.45 ppm (AA′BB′, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 115.3$, 124.0 (q, $J = 269.2$ Hz), 125.3 (q, $J = 3.9$ Hz), 126.4, 128.8 (q, $J = 32.0$ Hz), 130.6, 131.2, 132.0, 132.7, 140.8, 141.4, 154.9 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -63.1$ ppm; MS (FAB): m/z (%): 554 (9) $[M+2]^+$, 553 (41) $[M+1]^+$, 552 (100) M^+; elemental analysis: calcd (%) for $C_{32}H_{22}F_6O_2$: C 69.56, H 4.01; found: C 69.43, H 3.92.

(1*E*,3*E*,5*E*)-3,4-Bis(4-methoxyphenyl)-1,6-bis[4-(trifluoromethyl)phenyl]hexa-1,3,5-triene (1i): An oven-dried vial (3 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **8** (33 mg, 0.06 mmol), iodomethane (17 µL, 0.18 mmol), K_2CO_3 (18 mg, 0.13 mmol), and acetone (1 mL) at room temperature. The resulting solution was stirred at 60 °C for 24 h before quenching with saturated aqueous NH_4Cl (1 mL). The aqueous layer was extracted with dichloromethane (3 mL × 3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) to give **1i** (23 mg, 66 %) as a yellow solid. $R_f = 0.38$ (hexane/ethyl acetate 10:1); m.p.: 198.3–199.4 °C; IR (KBr): $\tilde{\nu} = 1611$, 1510, 1329, 1290, 1248, 1177, 1163, 1111, 1069, 1032, 1017, 970, 870, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.94$ (s, 6 H), 6.16 (d, $J = 15.6$ Hz, 2 H), 7.01–7.05 (m, 6 H), 7.21 (AA′BB′, 4 H), 7.26–7.28 (m, 4 H), 7.44 ppm (AA′BB′, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.4$, 113.7, 124.0 (q, $J = 269.4$ Hz), 125.3 (q, $J = 3.5$ Hz), 126.4, 128.7 (q, $J = 32.3$ Hz), 130.4, 131.1, 131.8, 132.9, 140.9 (d, $J = 1.6$ Hz), 141.5, 158.9 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -63.0$ ppm; MS (FAB): m/z (%): 582 (11) $[M+2]^+$, 581 (44) $[M+1]^+$, 580 (100) M^+; elemental analysis: calcd (%) for $C_{34}H_{26}F_6O_2$: C 70.34, H 4.51; found: C 70.04, H 4.59.

(1*E*,3*E*,5*E*)-3,4-Bis[4-(isopropoxy)phenyl]-1,6-bis[4-(trifluoromethyl)phenyl]hexa-1,3,5-triene (1j): An oven-dried vial (3 mL) equipped with a magnetic stirring bar and a rubber septum was charged with **8** (17 mg, 0.030 mmol), 2-iodopropane (9 µL, 0.09 mmol), K_2CO_3 (19 mg, 0.14 mmol), Bu_4NI (1.0 mg, 3 µmol), and acetone (1 mL) at room temperature. The resulting solution was stirred at 60 °C for 42 h before quenching with saturated aqueous NH_4Cl (1 mL). The aqueous layer was extracted with dichloromethane (3 mL × 3). The combined organic layer was washed with saturated aqueous NaCl (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure with a rotary evaporator. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) followed by recrystallization from hexane to give **1j** (5.0 mg, 26 %) as a yellow solid. $R_f = 0.60$ (hexane/ethyl acetate 5:1); m.p.: 197.4–199.2 °C; IR (KBr): $\tilde{\nu} = 1607$, 1508, 1327, 1240, 1165, 1123, 968, 953, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.45$ (d, $J = 6.0$ Hz, 12 H), 4.63–4.72 (m, 2 H), 6.18 (d, $J = 15.6$ Hz, 2 H), 7.00–7.07 (m, 6 H), 7.21–7.25 (m, 8 H), 7.44 ppm (AA′BB′, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22.3$, 70.0, 115.5, 124.0 (q, $J = 269.9$ Hz), 125.3 (q, $J = 3.8$ Hz), 126.4, 128.7 (q, $J = 32.0$ Hz), 130.2, 131.0, 131.9, 132.9, 141.0, 141.5, 157.2 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -63.0$ ppm; MS (FAB): m/z (%): 638 (12) $[M+2]^+$, 637 (51) $[M+1]^+$, 636 (100) M^+; elemental analysis: calcd (%) for $C_{38}H_{34}F_6O_2$: C 71.69, H 5.38; found: C 70.97, H 5.51.

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[13] Stereochemistry of major isomer **7** was determined as (1*E*,3*E*,5*E*) by X-ray analysis of its single crystal. (1*E*,3*E*,5*E*)-**7**: $C_{33}H_{21}Br_2Cl_3F_6$, crystal size $0.5\times0.5\times0.5$ mm^3, space group $P21/n$ (monoclinic), $a=14.829(10)$, $b=14.288(10)$, $c=16.931(12)$ Å, $\beta=114.036(13)°$, $V=3276(4)$ Å^3, $Z=4$, ρcalcd $=1.617$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha})=2.766$ mm^{-1}. Data were measured on a Bruker SMART APEX diffractometer ($\mathrm{Mo}_{K\alpha}$ radiation, $\lambda=0.71073$ Å) at 298 K, and the structure was solved by direct methods. Of 17506 reflections collected, 6080 were unique reflections ($R_{\mathrm{int}}=0.0355$); data/restraints/parameters 6080/0/397; final R indices [$I>2\sigma(I)$]: $R_1=0.0704$, $wR_2=0.1958$; R indices (all data): $R_1=0.1310$, $wR_2=0.2199$. CCDC 721572 contains the supplementary crystallographic data for (1*E*,3*E*,5*E*)-**7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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