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Fluorescence

Facile Preparation of α-Cyano-α,ω-Diaryloligovinylenes: A New Class of Color-Tunable Solid Emitters

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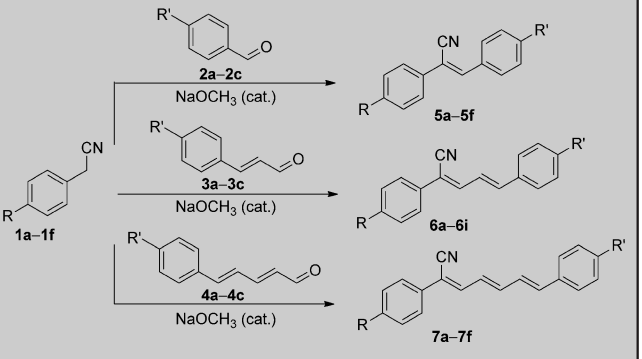
Abstract: An efficient Knoevenagel condensation reaction was used to construct a series of α-cyano-α,ω-diaryloligovinylenes, which show prominent fluorescence emission in the solid state. On investigating the effect of conjugation length on fluorescent properties, we found that the diene structure showed superior solid-state luminescence. Furthermore, the emission color could be adjusted by introducing donor or acceptor functional groups at the terminal aryl groups. Full-color emission in the visible region can be achieved by adding different functional groups to the α-cyano-α,ω-diaryldivinylene moiety. The structure–property relationships were elucidated and some observations such as the substitution position effects were discussed. These compounds have potential applications as full-color solid emissive candidates in material science and their simple structures allow them to be easily modified resulting in further interesting properties.

Introduction

Organic chromophores exhibiting efficient solid-state luminescence are strongly desired for practical applications such as organic light-emitting diodes (OLEDs), organic light-emitting field-effect transistors (OLEFETs), and organic solid-state lasers.[1] The design and synthesis of solid-emissive organic molecules remains a difficult task because it is necessary to conquer the commonly observed aggregation-caused quenching (ACQ) effect in the solid state.[2] Furthermore, motivated by the commercial potentials of full-color displays[3] and white-lighting emission,[4] it is highly desirable to realize multicolor emission with molecular mixtures of similar chemical structures. This is because it is relatively straightforward to obtain a series of structurally similar compounds with tunable emission by simple synthetic modification. Furthermore, microphase segregation, a detrimental problem in device performance owing to the mixing of emitting materials with significantly different chemical structures, can also be avoided with structurally similar analogues.[4b,5]

The "aggregation-induced emission (AIE)" term was coined by the research group of Tang[6] and this unleashed a flurry of researches in the discovery of solid-emissive fluorophores.[2b,7] However, similar structures with both cognate chemical skeletons and color tunable emission are still limited.[8] Herein, we report the preparation of solid-state color-tunable emitters by derivatizing cyano-substituted stilbenes to a homologous series of α-cyano-α,ω-diaryloligovinylene compounds **5a–5f**, **6a–6i**, and **7a–7f** with tunable fluorescent emitting bands (Table 1). In designing such multicolor solid-state emission structures, the following factors were taken into consideration: (i) the substituted (*E*)-diphenylethene segment is commonly found in AIE active structures;[2b,6b,9] (ii) introducing donor or

Table 1. Synthesis and structures of compounds **5a–5f**, **6a–6i**, and **7a–7f**.



Yield [%]			R	R′
5a (70)	**6a** (82)	**7a** (72)	H	H
5b (68)	**6b** (77)	**7b** (76)	OCH_3	H
5c (72)	**6c** (81)	**7c** (70)	H	OCH_3
5d (66)	**6d** (85)	**7d** (70)	OCH_3	OCH_3
5e (48)	**6e** (78)	**7e** (61)	OCH_3	NO_2
5f (55)	**6f** (82)	**7f** (65)	NO_2	OCH_3
	6g (73)		NEt_2	H
	6h (68)		CH_3	H
	6i (66)		NPh_2	H

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acceptor substituents to the terminal aryl rings is a facile way to obtain an emission wavelength shift by adjusting the energy gap or varying the degree of intramolecular charge transfer;[9] (iii) ethylene is the smallest π unit and introducing further vinylene units in the conjugation skeleton can generate a significant bathochromic shift of fluorescent emission;[10] (iv) the cyano group might not only render ground and excited states more distinct to produce large Stokes shift by desymmetrization of diphenylalkenes, but restrict intramolecular motions through a supramolecular C–H···N hydrogen-bond interaction in the solid or crystal state.[11]

Results and Discussion

Synthesis

By combining all the considerations above, we synthesized the target compounds **5a**–**5f**, **6a**–**6i**, and **7a**–**7f** through a Knoevenagel condensation reaction. Hence, *p*-substituted 2-phenylacetonitrile **1a**–**1f** and the *p*-substituted aromatic aldehyde **2a**–**2c**, **3a**–**3c**, and **4a**–**4c** were converted into α-cyano-α,ω-diaryloligovinylene **5a**–**5f**, **6a**–**6i**, and **7a**–**7f** in 48–85% yields in the presence of catalytic amount of $NaOCH_3$ (0.05–0.10 equiv) at room temperature with only *Z* configuration (Table 1). The products could be easily obtained by recrystallization and filtration. For compounds **5**–**7**, besides parent compound (**a**), one donor (**b** and **c**), two donors (**d**), and donor–π–acceptor (D–π–A) type (**e** and **f**) structures were synthesized, respectively, with selective donor and acceptor groups such as -OCH_3 and -NO_2. Substrates **4a**–**4c** were synthesized from **3a**–**3c** through a Wittig reaction, then reduced with diisobutylaluminum hydride (DIBAL-H), and subsequently oxidized with Dess–Martin periodinane (Scheme 1).

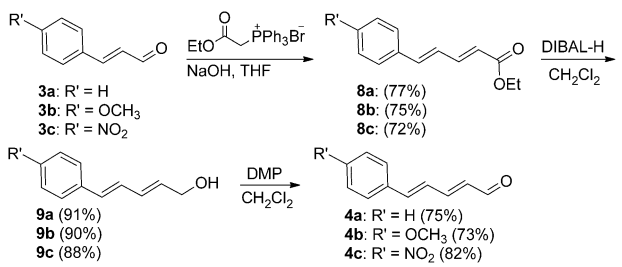
Table 2. Photophysical properties of samples **5a**–**5f**, **6a**–**6i**, and **7a**–**7f** as an amorphous powder and in solution.

Samples	λ_{max} [nm][a]	band gap [eV][b]	Solid[c]			Solution[f]		
			λ_{em} [nm][d]	Stokes shift [cm^{-1}]	Φ_f [%][e]	λ_{em} [nm][d]	Stokes shift [cm^{-1}]	Φ_f [%][e]
5a	313	3.55	ND		–[g]	ND		–
5b	333	3.33	425	6501	44.2	ND		–
5c	320	3.36	ND		–	ND		–
5d	328	3.27	412	6216	28.4	430	7231	–
5e	357	2.92	590	11062	1.9	507	8287	7.5
5f	359	2.87	565	10156	25.2	ND		–
6a	338	3.22	465	8080	14.3	ND		–
6b	358	3.05	490	7525	70.2	ND		–
6c	365	2.94	495	7195	0.8	470	6121	–
6d	368	2.92	485	6555	53.0	ND		–
6e	396	2.72	590	8303	13.2	522	6095	62.1
6f	394	2.64	614	9093	1.9	567	7744	3.0
6g	422	2.62	572	6214	45.2	510	4089	78.0
6h	339	3.21	479	8621	30.9	400	4499	3.2
6i	417	2.61	540	5462	25.5	549	5766	69.3
7a	370	2.92	526	8016	0.86	506	7264	–
7b	381	2.84	518	6942	13.0	507	6523	–
7c	390	2.72	538	7053	5.55	544	7259	–
7d	395	2.71	564	7586	0.6	538	6729	–
7e	408	2.59	635	8762	0.4	553	6427	91.7
7f	425	2.43	684	8910	0.23	631	7682	–

[a] Measured in EtOH (10 μM). [b] Calculated from UV/Vis absorption. [c] Measured using amorphous powder. [d] 368–454 nm was used as excitation wavelength based on excitation spectrum of each compound. [e] Absolute quantum yield. [f] Measured in THF (10 μM). [g] Quantum yield was not measured because of low fluorescence. ND = fluorescence not detectable.

Photophysical Properties

With all the samples in hand, the UV/Vis absorptions were first measured in diluted solution (Table 2, see Figure S1–S3 in the Supporting Information). It was observed that the maximum absorption wavelength ranges from 313 nm to 425 nm, and both extension of conjugation length with additional double bond(s) and incorporation of electron-donating or electron-withdrawing functional groups could contribute to the absorption bathochromic shift. This broad scope of absorbance is indeed favorable for shifting the emission wavelength. Accordingly, the band gap energy became narrower with additional conjugation or by introducing donor–acceptor functional groups (Table 2). The D–π–A substitution pattern showed the largest bathochromic absorbance and smallest band gap energy.



Scheme 1. Synthesis of substrates **4a**–**4c**.

Next, the fluorescence properties including fluorescence emission and fluorescence quantum yield were investigated both in amorphous powder and in diluted solution (Table 2). In brief, this series of α-cyano-α,ω-diaryloligovinylenes exhibited an AIE effect. Most samples showed significant fluorescent emission in the solid state. However, most compounds showed very weak or almost no fluorescence in diluted solution because of the flexible π systems except several D–π–A type compounds **5e**, **6e**, **6g**, **6i**, and **7e**. The maximum emission wavelengths of the solid powder extend from 412 nm (**5d**) to 684 nm (**7f**) with large Stokes shifts (Table 2, 5462–11062 cm^{-1}). To our delight, the fluorescence emission range of these α-cyano-α,ω-diaryloligovinylene derivatives in the solid state covered the whole visible region.

The fluorescence characteristics are summarized: (i) The homologous series with one ethylene unit distinction displayed

a large difference in luminous efficiency. For the three conjugated groups, the diene (except **6c** and **6f**) gave superior luminous efficiency compared to that of the monoene and triene derivatives in most cases (for example, compound **5a** was not fluorescent in the solid state, while compound **6a** showed blue emission with a fluorescence quantum yield of 14.3%, and the emissive efficiency of **7a** was reduced to less than 1%), which suggests that conjugation length is important for high-efficiency fluorescence for this type of compound. Therefore, full-color solid emission in the visible region was achieved by simply modifying the diene skeleton with donors or acceptors (Figure 1 and Figure S5, see the Supporting Information). (ii) Regioisomers were found to show dramatically different fluorescent efficiency. The structures with one donor

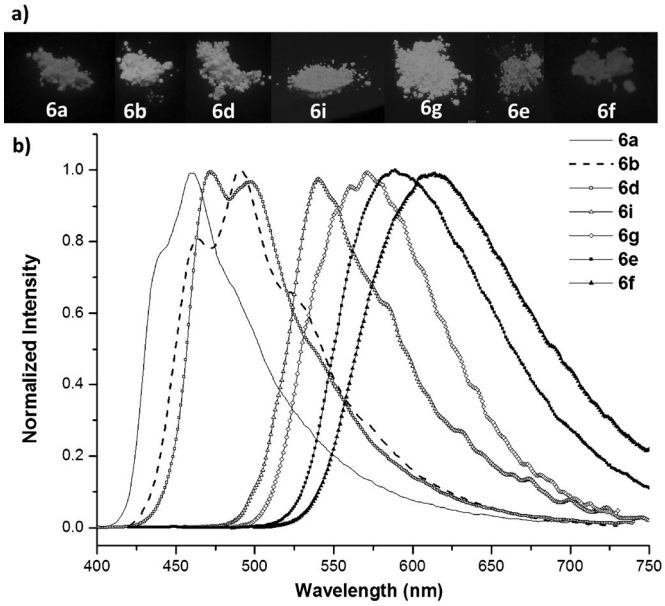


Figure 1. a) Photographs of samples **6a**, **6b**, **6i**, and **6d**–**6g** (amorphous powder) under 365 nm UV light. b) Normalized fluorescence spectra of corresponding samples in the solid state.

group (-OCH_3) connected to the phenyl ring (Table 1) had different fluorescent efficiencies (comparison of compounds **5b**, **6b**, and **7b** to **5c**, **6c**, and **7c** respectively). The high fluorescence quantum yield could be maintained when the -OCH_3 was changed to an electron-donating group such as -NEt_2, -CH_3, -NPh_2 (**6g**, 45.2%; **6h**, 30.9%; **6i**, 25.5%). (iii) The D–π–A type structures exhibited long wavelength emission with decreased fluorescence quantum yields; some of them were strongly fluorescent in dilute solution (compounds **5e**, **6e**, **6i**, and **7e**).

Analysis of Structure–Property Relationships

To understand the above emission features of these compounds and better tune the fluorescence properties, compounds **6b**, **6c**, and **6e** were crystallized in a CH_2Cl_2/hexane mixed solvent[12] to afford single crystals[7d] and subsequently subjected to X-ray crystallographic analysis (Figure 2–4, see Figure S8–S10 and Table S1 in the Supporting Information). The corresponding frontier orbital levels of the three compounds were estimated by DFT calculation based on crystal structure data (Figure 5 and Figure S11, see the Supporting Information).

The crystal structure of compound **6b** is shown in Figure 2 and Figure S8 (see the Supporting Information). It was found that the whole π conjugated skeleton displayed a slightly twisted framework, and from the side view (Figure 2b), the dihedral angles between two phenyl rings and diene fragment

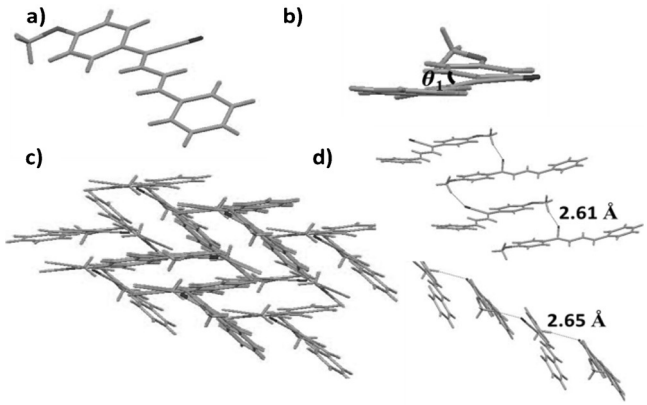


Figure 2. a) Single crystal structure of compound **6b** from the b) side view and c) packing view. d) The C–H···N hydrogen-bond interaction in crystal packing.

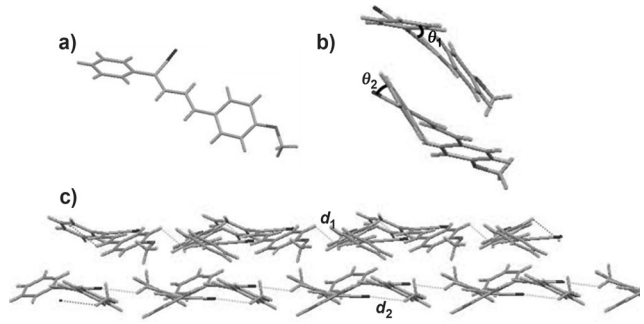


Figure 3. a) Single crystal structure of compound **6c** from the b) side view and c) packing view.

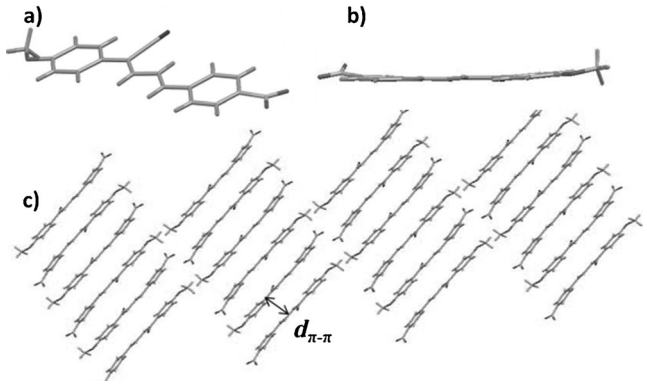


Figure 4. a) Single crystal structure of compound **6e** from the b) side view and c) packing view.

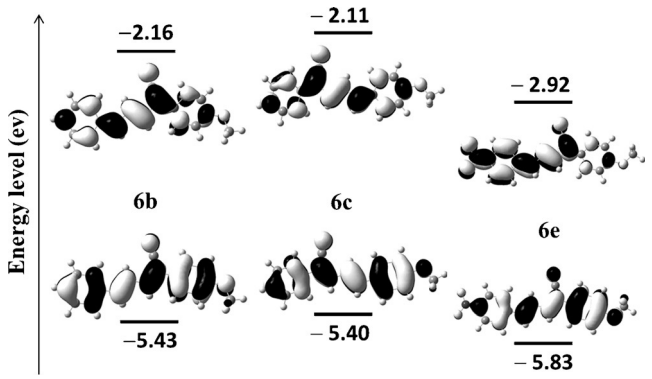


Figure 5. Molecular orbitals and energy levels of **6b**, **6c**, and **6e** obtained from DFT calculations [B3LYP/6-31G (d) level] by Gaussian 09 program[13]. The lower and upper orbital diagrams represent HOMO and LUMO, respectively.

are 13.1° and 13.4°, respectively ($\theta_1 = 13.1°$). This non-planar structure could potentially suppress the intermolecular face-to-face packing. It was noted that the cyano group could interact with one of the hydrogen atoms in -OCH_3 to form an intermolecular C–H···N hydrogen bond, and the interaction distances of two arrangement directions are 2.61 Å and 2.65 Å, respectively (Figure 2d). The twisted molecular plane and supramolecular hydrogen-bond interaction led to a cross-like packing arrangement (Figure 2c), which can effectively minimize the quenching in fluorescence caused by solid aggregation to give a 70.2% fluorescence quantum yield in the solid state.

By comparison, compound **6c** with a similar structure to its regioisomer **6b**, however, gave only 0.8% fluorescence quantum yield (70.2% for **6b**). This regioisomeric effect could be explained by the over twisted molecular configuration. In the single crystal structure (Figure 3 and Figure S9 in the Supporting Information), two conformations were observed in one structure that showed an axial chirality relationship, in which dihedral angles θ_1 and θ_2 could be considered as phenyl ring rotating in a different direction. The whole π system is highly twisted and the dihedral angle between the phenyl ring and diene is 38° (θ_1 and θ_2), and the dihedral angle between two phenyl rings is 51°. Such a non-planar form intensely paralyzed the reasonable emission configuration, and this resulted in weaker fluorescence. Meanwhile, the stronger warping structure was consistent with HOMO–LUMO gap increasing in packing state: in diluted solution, **6c** gave narrower band gap than **6b** (Table 2, 2.94 to 3.05 eV). However, in crystal packing, the gap value of **6c** was slightly larger (Figure 5 and Figure S11 in the Supporting Information, 3.29 to 3.27 eV). Also, two types of intermolecular interaction resulted in different packing patterns (Figure 3c): the upper layer was induced by CH···CH interaction with distance $d_1 = 2.40$ Å; the lower layer was induced by C–H···N interaction, which became weaker compared to **6b** ($d_2 = 2.74$ Å). The axial chirality was produced in this process.

As expected, with the D–π–A substitution pattern, compound **6e** exhibited a much smaller band gap than **6b** and **6c** by dramatically lowering the LUMO orbital energy through introducing an electron-withdrawing group (Figure 5, $\Delta E =$ 2.91 eV), by which the emission bands of compound **6e** in solid state was shifted to orange region ($\lambda_{em} = 590$ nm). The single crystal structure revealed that the π-skeleton of compound **6e** had an essentially planar configuration and lamellar stacking was formed in space (Figure 4 and Figure S10 in the Supporting Information). Furthermore, different types of supramolecular interactions were detected. First, O···N and O···H interactions were observed in nitro-nitro groups and nitro-methoxy groups, and the interaction distances were 2.94 Å and 2.70 Å, respectively. Next, instead of a OCH_2-H···N hydrogen-bond interaction, the N in the cyano group also interacted with H in alkene to form C–H···N interaction with a much closer distance (2.56 Å). More importantly, an intermolecular π–π interaction was detected ($d_{\pi-\pi} = 3.38$ Å), which tended to form excimers. Thus, the luminous efficiency was consumed by densely aggregation.

Conclusions

In conclusion, three types of substituted α-cyano-α,ω-diaryloligovinylenes from ethylene to triene were efficiently synthesized through a Knoevenagel condensation reaction. It was found that the solid-fluorescent emission wavelength could be tuned by the conjugation length and different substitutent variations. The emission covered the whole visible region with center wavelength ranging from 412 nm to 684 nm in the solid state. Notably, the diene moieties showed full-color displays in powder form by simply introducing donor or acceptor functional groups and switching their positions. Some structure–property relationships were rationalized by a combination of X-ray crystallography and DFT calculations. Comparing to other full-color display compounds, the advantages of these structures are their simple preparation and small size, which would provide more potential for practical applications. Meanwhile, investigations to suppress the densely fluorescence quenching are in process.

Experimental Section

General Information

All reactions that required anhydrous conditions were carried out using standard procedures under argon. Commercially available substrates such as *p*-substituted 2-phenyl acetonitriles **1a**–**1f**, *p*-substituted aromatic aldehyde **2a**–**2c**, and **3a**–**3c** were used as received. The solvents were dried by distillation over the appropriate drying reagents. The petroleum ether (PE) used had a boiling range of 60–90 °C. Reactions were monitored by TLC on silica gel GF 254 plates. Column chromatography was generally performed through silica gel (200–300 mesh). Melting points were recorded with an X-4 microscope melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C), as were the DEPT 135 experiments. Chemical shift values are given in ppm and coupling constants (*J*) in Hertz. Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference ($CDCl_3$: $\delta_{TMS} = 0$, $\delta_C = 77.0$ ppm; [D_6]DMSO: $\delta_H = 2.50$, $\delta_C = 39.5$ ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), ddd (doublet of doublet of doublets). High resolution mass spectra were obtained

on a Bruker Daltonics APEX III 47e FT-ICR mass spectrometer or on a Fisons VG Autospec double focusing sector-field instrument by using electrospray ionization (ESI) techniques. UV/Vis absorptions were carried out on a UV-Cary100 spectrophotometer. The fluorescence spectra and the fluorescence quantum yields were measured from the solution and powder form using the Edinburgh Instruments (FLS920). Single crystal X-ray diffraction measurements were performed with a Bruker X8 APEX diffractometer working with graphite monochromated $Mo_{K\alpha}$ and $Cu_{K\alpha}$ radiation.

The Preparation and Characterization Data of Compounds 5a–5f, 6a–6i, and 7a–7f(*Z*)-2,3-Diphenylacrylonitrile (5a):

To a solution of 2-phenylacetonitrile (**1a**, 462 μL, $d=1.02\ g\,mL^{-1}$, 4.00 mmol) in EtOH (20 mL) was added benzaldehyde **2a** (404 μL, $d=1.05\ g\,mL^{-1}$, 4.00 mmol) and fresh prepared 1 M $NaOCH_3$ solution in methanol (0.4 mL, 0.40 mmol) with stirring. Then the mixture was stirred at room temperature for around 10 h, and the precipitate formed. The reaction mixture was placed at 0 °C for a while before filtration to afford a white solid. The solid was washed with cold EtOH to provide the title compound (575 mg, 70%). M.p. 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.91$–7.89 (m, 2H), 7.70–7.68 (m, 2H), 7.55 (s, 1H), 7.50–7.38 ppm (m, 6H). The data were in agreement with the literature.[14]

Compounds **5b**–**5f** were synthesized using *p*-substituted 2-phenyl acetonitriles **1a**–**1c** and aldehydes **2a**–**2c** as substrates according to the procedure given above for compound **5a** (When nitro-substituted 2-(4-nitrophenyl)acetonitrile (**1c**) was used, $NaOCH_3$ (0.05 equiv) was required). When the solubility for some substrates was not good in EtOH, THF was added to increase the solubility.

(*Z*)-2-(4-Methoxyphenyl)-3-phenylacrylonitrile (5b):

The title compound **5b** was prepared from **1b** (544 μL, $d=1.08\ g\,mL^{-1}$, 4.00 mmol) and **2a** (404 μL, $d=1.05\ g\,mL^{-1}$, 4.00 mmol) as a white solid (639 mg, 68%). M.p. 87–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.87$ (d, $J=7.6$ Hz, 2H), 7.62 (d, $J=8.8$ Hz, 2H), 7.48–7.42 (m, 4H), 6.97 (d, $J=8.8$ Hz, 2H), 3.86 ppm (s, 3H). The data were in agreement with the literature.[14]

(*Z*)-2-Phenyl-3-(4-methoxyphenyl)acrylonitrile (5c):

The title compound **5c** was prepared from **1a** (462 μL, $d=1.02\ g\,mL^{-1}$, 4.00 mmol) and **2b** (486 μL, $d=1.12\ g\,mL^{-1}$, 4.00 mmol) as a white solid (677 mg, 72%). M.p. 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.89$ (d, $J=8.8$ Hz, 2H), 7.66 (d, $J=8.8$ Hz, 2H), 7.47–7.35 (m, 4H), 6.98 (d, $J=8.8$ Hz, 2H), 3.87 ppm (s, 3H). The data were in agreement with the literature.[14]

(*Z*)-2,3-Bis(4-methoxyphenyl)acrylonitrile (5d):

The title compound **5d** was prepared from **1b** (544 μL, $d=1.08\ g\,mL^{-1}$, 4.00 mmol) and **2b** (486 μL, $d=1.12\ g\,mL^{-1}$, 4.00 mmol) as a light green solid (700 mg, 66%). M.p. 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.85$ (d, $J=8.8$ Hz, 2H), 7.58 (d, $J=8.8$ Hz, 2H), 7.36 (s, 1H), 6.97 (d, $J=8.8$ Hz, 2H), 6.95 (d, $J=8.8$ Hz, 2H), 3.87 (s, 3H), 3.85 ppm (s, 3H). The data were in agreement with the literature.[14]

(*Z*)-2-(4-Methoxyphenyl)-3-(4-nitrophenyl)acrylonitrile (5e):

The title compound **5e** was prepared from **1b** (408 μL, $d=1.08\ g\,mL^{-1}$, 3.00 mmol) and **2c** (453 mg, 3.00 mmol) as an orange solid (403 mg, 48%). M.p. 94–96 °C; ^{1}H NMR (400 MHz, [D_6]DMSO): $\delta=8.38$ (d, $J=8.8$ Hz, 2H), 8.12 (d, $J=8.8$ Hz, 2H), 8.11 (s, 1H), 7.77 (d, $J=8.8$ Hz, 2H), 7.11 (d, $J=8.8$ Hz, 2H), 3.84 ppm (s, 3H). The data were in agreement with the literature.[14]

(*Z*)-3-(4-Methoxyphenyl)-2-(4-nitrophenyl)acrylonitrile (5f):

The title compound **5f** was prepared from **1c** (648 mg, 4.00 mmol) and **2b** (486 μL, $d=1.12\ g\,mL^{-1}$, 4.00 mmol) as a yellow solid (616 mg, 55%). M.p. 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.30$ (d, $J=8.8$ Hz, 2H), 7.96 (d, $J=8.8$ Hz, 2H), 7.82 (d, $J=8.8$ Hz, 2H), 7.61 (s, 1H), 7.02 (d, $J=8.8$ Hz, 2H), 3.90 ppm (s, 3H). The data were in agreement with the literature.[15]

Compounds **6a**–**6i** were synthesized using *p*-substituted 2-phenylacetonitriles **1a**–**1f** and aldehydes **3a**–**3c** as substrates according to the procedure given above for compound **5a** [When nitro-substituted 2-(4-nitrophenyl)acetonitrile (**1c**) was used, $NaOCH_3$ (0.05 equiv) was required. When the solubility for some substrates was not good in EtOH, THF was added to increase the solubility.

(2*Z*,4*E*)-2,5-Diphenylpenta-2,4-dienenitrile (6a):

The title compound **6a** was prepared from **1a** (462 μL, $d=1.02\ g\,mL^{-1}$, 4.00 mmol) and **3a** (504 μL, $d=1.05\ g\,mL^{-1}$, 4.00 mmol) as a white solid (758 mg, 82%). M.p. 116–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.63$ (d, $J=7.6$ Hz, 2H), 7.56 (d, $J=7.2$ Hz, 2H), 7.45–7.35 (m, 8H), 7.01–6.99 ppm (m, 1H). The data were in agreement with the literature.[16]

(2*Z*,4*E*)-2-(4-Methoxyphenyl)-5-phenylpenta-2,4-dienenitrile (6b):

The title compound **6b** was prepared from **1b** (544 μL, $d=1.08\ g\,mL^{-1}$, 4.00 mmol) and **3a** (504 μL, $d=1.05\ g\,mL^{-1}$, 4.00 mmol) as a green solid (804 mg, 77%). M.p. 159–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.58$–7.53 (m, 4H), 7.40–7.31 (m, 5H), 6.99–6.93 (m, 3H), 3.85 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 160.4 (C), 140.0 (CH), 139.5 (CH), 135.9 (C), 129.3 (CH), 128.9 (CH), 127.4 (CH), 127.0 (CH), 125.8 (C), 125.3 (CH), 117.1 (C), 114.5 (CH), 112.7 (C), 55.4 ppm (CH_3); HRMS (ESI): *m/z* calcd for $C_{18}H_{15}NO+H^+$: 262.1226 [$M+H^+$]; found: 262.1223.

(2*Z*,4*E*)-5-(4-Methoxyphenyl)-2-phenylpenta-2,4-dienenitrile (6c):

The title compound **6c** was prepared from **1a** (347 μL, $d=1.02\ g\,mL^{-1}$, 3.00 mmol) and **3b** (486 mg, 3.00 mmol) as a green solid (634 mg, 81%). M.p. 136–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.63$–7.61 (m, 2H), 7.51 (d, $J=8.8$ Hz, 2H), 7.44–7.39 (m, 3H), 7.35 (d, $J=7.2$ Hz, 1H) 7.31–7.24 (m, 1H), 6.98 (d, $J=11.2$ Hz, 1H), 6.92 (d, $J=8.8$ Hz, 2H), 3.85 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.9$ (C), 142.1 (CH), 141.0 (CH), 133.5 (C), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.6 (C), 125.5 (CH), 123.2 (CH), 117.3 (C), 114.5 (CH), 111.6 (C), 55.4 ppm (CH_3). The data were in agreement with the literature.[16]

(2*Z*,4*E*)-2,5-Bis(4-methoxyphenyl)penta-2,4-dienenitrile (6d):

The title compound **6d** was prepared from **1b** (408 μL, $d=1.08\ g\,mL^{-1}$, 3.00 mmol) and **3b** (486 mg, 3.00 mmol) as a green solid (742 mg, 85%). M.p. 161–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.53$ (d, $J=8.8$ Hz, 2H), 7.48 (d, $J=8.8$ Hz, 2H), 7.29–7.20 (m, 2H), 6.95–6.90 (m, 5H), 3.84 (s, 3H), 3.84 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.6$ (C), 160.2 (C), 140.0 (CH), 139.8 (CH), 128.9 (CH), 128.8 (C), 126.8 (CH), 126.1 (C), 123.3 (CH), 117.4 (C),

114.4 (CH), 114.3 (CH), 111.3 (C), 55.4 (CH_3), 55.3 ppm (CH_3); HRMS (ESI): *m/z* calcd for $C_{19}H_{17}NO_2+H^+$: 292.1332 [$M+H^+$]; found: 292.1328.

(2*Z*,4*E*)-2-(4-Methoxyphenyl)-5-(4-nitrophenyl)penta-2,4-dienenitrile (6e):

The title compound **6e** was prepared from **1b** (408 μL, $d=1.08\ g\,mL^{-1}$, 3.00 mmol) and **3c** (531 mg, 3.00 mmol) as an orange red solid (716 mg, 78%). M.p. 166–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.21$ (d, $J=8.8$ Hz, 2H), 7.64 (d, $J=8.8$ Hz, 2H), 7.57 (d, $J=8.8$ Hz, 2H), 7.53–7.43 (m, 1H), 7.31–7.27 (m, 1H), 7.00–6.93 (m, 3H), 3.85 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=161.0$ (C), 147.6 (C), 142.2 (C), 137.7 (CH), 136.6 (CH), 129.3 (CH), 127.7 (CH), 127.3 (CH), 125.2 (C), 124.2 (CH), 116.7 (C), 115.8 (C), 114.6 (CH), 55.5 ppm (CH_3); HRMS (ESI): *m/z* calcd for $C_{18}H_{14}N_2O_3+H^+$: 307.1077 [$M+H^+$]; found: 307.1075.

(2*Z*,4*E*)-5-(4-Methoxyphenyl)-2-(4-nitrophenyl)penta-2,4-dienenitrile (6f):

The title compound **6f** was prepared from **1c** (486 mg, 3.00 mmol) and **3b** (486 mg, 3.00 mmol) as a red solid (753 mg, 82%). M.p. 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.28$ (d, $J=8.8$ Hz, 2H), 7.77 (d, $J=9.2$ Hz, 2H), 7.56 (d, $J=11.2$ Hz, 1H), 7.55 (d, $J=8.8$ Hz, 2H), 7.32 (d, $J=11.2$ Hz, 1H), 7.12 (d, $J=13.2$ Hz, 1H), 6.95 (d, $J=8.8$ Hz, 2H), 3.87 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=161.5$ (C), 147.2 (C), 145.5 (CH), 144.3 (CH), 139.6 (C), 129.5 (CH), 128.0 (C), 125.8 (CH), 124.3 (CH), 122.4 (CH), 116.4 (C), 114.5 (CH), 109.0 (C), 55.4 ppm (CH_3). The data were in agreement with the literature.[16]

(2*Z*,4*E*)-2-[4-(Diethylamino)phenyl]-5-phenylpenta-2,4-dienenitrile (6g):

The title compound **6g** was prepared from **1d** (131 mg, 0.70 mmol) and **3a** (88 μL, $d=1.05\ g\,mL^{-1}$, 0.70 mmol) as a yellow solid (154 mg, 73%). M.p. 106–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.53$–7.47 (m, 4H), 7.40–7.27 (m, 4H), 7.19 (d, $J=11.2$ Hz, 1H), 6.88 (d, $J=15.6$ Hz, 1H), 6.66 (d, $J=8.8$ Hz, 2H), 3.39 (q, $J=7.2$ Hz, 4H), 1.19 ppm (t, $J=7.2$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=148.2$ (C), 137.8 (CH), 136.4 (C), 136.0 (CH), 128.8 (CH), 128.7 (CH), 127.1 (CH), 126.9 (CH), 125.8 (CH), 120.0 (C), 117.4 (C), 113.4 (C), 111.5 (CH), 44.4 (CH_2), 12.6 ppm (CH_3); HRMS (ESI): *m/z* calcd for $C_{21}H_{22}N_2+H^+$: 303.1856 [$M+H^+$]; found: 303.1850.

(2*Z*,4*E*)-5-Phenyl-2-(*p*-tolyl)penta-2,4-dienenitrile (6h)

The title compound **6h** was prepared from **1e** (527 μL, $d=0.994\ g\,mL^{-1}$, 4.00 mmol) and **3a** (504 μL, $d=1.05\ g\,mL^{-1}$, 4.00 mmol) as a yellow solid (666 mg, 68%). M.p. 136–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.56$–7.50 (m, 4H), 7.42–7.30 (m, 5H), 7.22 (d, $J=8.0$ Hz, 2H), 7.03–6.94 (m, 1H), 2.38 ppm (s, 3H). The data were in agreement with the literature.[17]

(2*Z*,4*E*)-2-(4-(Diphenylamino)phenyl)-5-phenylpenta-2,4-dienenitrile (6i)

The title compound **6i** was prepared from **1f** (284 mg, 1.00 mmol) and **3a** (126 μL, $d=1.05\ g\,mL^{-1}$, 1.00 mmol) as a yellow solid (263 mg, 66%). M.p. 155–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.53$ (d, $J=7.2$ Hz, 2H), 7.46 (d, $J=8.8$ Hz, 2H), 7.42–7.23 (m, 9H), 7.15–7.02 (m, 8H), 6.95 ppm (d, $J=15.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=148.7$ (C), 147.0 (C), 139.8 (CH), 139.1 (CH), 136.0 (C), 129.4 (CH), 129.2 (CH), 128.9 (CH), 127.3 (CH), 126.43 (CH), 126.37 (C), 125.4 (CH), 125.0 (CH), 123.8 (CH), 122.4 (CH), 117.1 (C), 112.8 ppm (C); HRMS (ESI): *m/z* calcd for $C_{29}H_{22}N_2+H^+$: 399.1856 [$M+H^+$]; found: 399.1851.

Compounds **7a**–**7f** were synthesized using *p*-substituted 2-phenyl acetonitriles **1a**–**1c** and aldehydes **4a**–**4c** as substrates according to the procedure given above for compound **5a** (When nitro-substituted 2-(4-nitrophenyl)acetonitrile (**1c**) was used, $NaOCH_3$ (0.05 equiv) was required. When the solubility for some substrates was not good in EtOH, THF was added to increase the solubility.

(2*Z*,4*E*,6*E*)-2,7-Diphenylhepta-2,4,6-trienenitrile (7a):

The title compound **7a** was prepared from **1a** (176 μL, $d=1.02\ g\,mL^{-1}$, 1.53 mmol) and **4a** (158 mg, 1.00 mmol) as a green solid (185 mg, 72%). M.p. 136–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.62$ (d, $J=7.2$ Hz, 2H), 7.60–7.26 (m, 9H), 7.04–6.97 (m, 2H), 6.94–6.78 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=141.5$ (CH), 141.2 (CH), 137.7 (CH), 136.4 (C), 133.3 (C), 129.2 (CH), 129.0 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 128.0 (CH), 127.0 (CH), 125.5 (CH), 117.0 (C), 112.5 ppm (C); HRMS (ESI): *m/z* calcd for $C_{19}H_{15}N+H^+$: 258.1277 [$M+H^+$]; found: 258.1278.

(2*Z*,4*E*,6*E*)-2-(4-Methoxyphenyl)-7-phenylhepta-2,4,6-trienenitrile (7b):

The title compound **7b** was prepared from **1b** (117 μL, $d=1.08\ g\,mL^{-1}$, 0.86 mmol) and **4a** (136 mg, 0.86 mmol) as a green solid (188 mg, 76%). M.p. 153–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.55$ (d, $J=8.8$ Hz, 2H), 7.46 (d, $J=7.2$ Hz, 2H), 7.38–7.34 (m, 2H), 7.29 (d, $J=7.2$ Hz, 1H), 7.22 (d, $J=11.2$ Hz, 1H), 7.03–6.91 (m, 4H), 6.83–6.75 (m, 2H), 3.85 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.3$ (C), 140.3 (CH), 139.1 (CH), 137.0 (CH), 136.5 (C), 129.4 (CH), 128.8 (CH), 128.5 (CH), 128.2 (CH), 126.9 (CH), 126.8 (CH), 125.9 (C), 117.2 (C), 114.4 (CH), 112.1 (C), 55.4 ppm (CH_3); HRMS (ESI): *m/z* calcd for $C_{20}H_{17}NO+H^+$: 288.1383 [$M+H^+$]; found: 288.1383.

(2*Z*,4*E*,6*E*)-7-(4-Methoxyphenyl)-2-phenylhepta-2,4,6-trienenitrile (7c):

The title compound **7c** was prepared from **1a** (102 μL, $d=1.02\ g\,mL^{-1}$, 0.88 mmol) and **4b** (113 mg, 0.60 mmol) as green solid (121 mg, 70%). M.p. 145–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.60$ (d, $J=7.6$ Hz, 2H), 7.43–7.39 (m, 4H), 7.36–7.32 (m, 2H), 6.95–6.73 (m, 6H), 3.84 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.2$ (C), 142.0 (CH), 141.5 (CH), 137.5 (CH), 133.4 (C), 129.3 (C), 129.0 (CH), 128.8 (CH), 128.4 (CH), 128.2 (CH), 126.0 (CH), 125.5 (CH), 117.2 (C), 114.4 (CH), 111.7 (C), 55.3 ppm (CH_3); HRMS (ESI): *m/z* calcd for $C_{20}H_{17}NO+H^+$: 288.1383 [$M+H^+$]; found: 288.1382.

(2*Z*,4*E*,6*E*)-2,7-Bis(4-methoxyphenyl)hepta-2,4,6-trienenitrile (7d):

The title compound **7d** was prepared from **1b** (120 μL, $d=1.08\ g\,mL^{-1}$, 0.88 mmol) and **4b** (113 mg, 0.60 mmol) as a green solid (133 mg, 70%). M.p. 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.53$ (d, $J=8.8$ Hz, 2H), 7.40 (d, $J=8.8$ Hz, 2H), 7.21 (d, $J=11.2$ Hz, 1H), 6.94–6.86 (m, 6H), 6.83–6.70 (m, 2H), 3.84 (s, 3H), 3.83 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.1$ (C), 160.0 (C), 140.8 (CH), 139.5 (CH), 136.8 (CH), 129.4 (C), 128.4 (CH), 128.3 (CH), 126.8 (CH), 126.2 (CH), 126.0 (C), 117.3 (C), 114.4 (CH), 114.3 (CH), 111.3 (C), 55.4 (CH_3), 55.3 ppm (CH_3); HRMS (ESI): *m/z* calcd for $C_{21}H_{19}NO_2+H^+$: 318.1489 [$M+H^+$]; found: 318.1488.

(2*Z*,4*E*,6*E*)-2-(4-Methoxyphenyl)-7-(4-nitrophenyl)hepta-2,4,6-trienenitrile (7e):

The title compound **7e** was prepared from **1b** (145 μL, d= 1.08 g mL^{-1}, 1.07 mmol) and **4c** (180 mg, 0.89 mmol) as a red solid (180 mg, 61%). M.p. 201–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.22 (d, J=8.8 Hz, 2H), 7.67–7.51 (m, 4H), 7.24 (d, J=11.6 Hz, 1H), 7.16–7.02 (m, 2H), 6.95 (d, J=8.8 Hz, 2H), 6.83–6.77 (m, 2H), 3.86 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=160.7 (C), 147.1 (C), 143.0 (C), 138.7 (CH), 138.1 (CH), 133.8 (CH), 132.5 (CH), 132.2 (CH), 127.2 (CH), 125.6 (C), 124.2 (CH), 116.8 (C), 114.6 (CH), 114.3 (C), 55.5 ppm (CH_3), one overlapping Ar-CH resonance; HRMS (ESI): m/z calcd for $C_{20}H_{16}N_2O_3$+H$^+$: 333.1234 [M+H$^+$]; found: 333.1234.

(2*Z*,4*E*,6*E*)-7-(4-Methoxyphenyl)-2-(4-nitrophenyl)hepta-2,4,6-trienenitrile (7f):

The title compound **7f** was prepared from **1c** (86 mg, 0.53 mmol) and **4b** (100 mg, 0.53 mmol) as a dark red solid (114 mg, 65%). M.p. 195–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.27 (d, J=9.2 Hz, 2H), 7.75 (d, J=9.2 Hz, 2H), 7.52–7.48 (m, 1H), 7.44 (d, J=8.8 Hz, 2H), 7.00–6.82 (m, 6H), 3.85 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=160.6 (C), 147.3 (C), 145.2 (CH), 144.8 (C), 139.8 (CH), 139.7 (C), 128.9 (CH), 128.8 (CH), 127.5 (CH), 125.9 (CH), 125.6 (CH), 124.3 (CH), 116.3 (C), 114.4 (CH), 109.0 (C), 55.4 ppm (CH_3); HRMS (ESI): m/z calcd for $C_{20}H_{16}N_2O_3$+H$^+$: 333.1234 [M+H$^+$]; found: 333.1234.

(2*E*,4*E*)-Ethyl-5-phenylpenta-2,4-dienoate (8a):

Compound **8a** was synthesized from **3a** according to a literature procedure.[18] To a solution of (2-ethoxy-2-oxoethyl) triphenylphosphonium salt (2.57 g, 6.00 mmol) in THF (30 mL) was added NaOH (240 mg, 6.00 mmol) with some drops of water. The mixture was stirred at room temperature for 10 min, then cinnamaldehyde (**3a**, 660 mg, 5.00 mmol) was added to the above reaction mixture. The reaction system became clear and stirred until no aldehyde remained. The solvent was removed under vacuum. The residue was purified by silica-gel flash chromatography to give the title compound as a colorless liquid (778 mg, 77%). R_f=0.58 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.48–7.41 (m, 3H), 7.38–7.28 (m, 3H), 6.93–6.83 (m, 2H), 5.99 (d, J=15.3 Hz, 1H), 4.23 (q, J=7.2 Hz, 2H), 1.32 ppm (t, J=7.2 Hz, 3H). The data were in agreement with the literature.[18]

Compounds **8b** and **8c** were synthesized using **3b** and **3c** as substrates, respectively, according to the procedure given above for compound **8a**.

(2*E*,4*E*)-Ethyl-5-(4-methoxyphenyl)penta-2,4-dienoate (8b):

The title compound **8b** was prepared from **3b** (810 mg, 5.00 mmol) and (2-ethoxy-2-oxoethyl)triphenylphosphonium salt (2.57 g, 6.00 mmol) as white solid (870 mg, 75%). R_f=0.52 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.47–7.40 (m, 3H), 6.91–6.88 (m, 3H), 6.78–6.72 (q, 1H), 5.94 (d, J=15.6 Hz, 1H), 4.22 (q, J=7.2 Hz, 2H), 3.83 (s, 3H), 1.31 ppm (t, J=7.2 Hz, 3H). The data were in agreement with the literature.[19]

(2*E*,4*E*)-Ethyl-5-(4-nitrophenyl)penta-2,4-dienoate (8c):

The title compound **8c** was prepared from **3c** (885 mg, 5.00 mmol) and (2-ethoxy-2-oxoethyl)triphenylphosphonium salt (2.57 g, 6.00 mmol) as a white solid (889 mg, 72%). R_f=0.75 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.22 (d, J=8.8 Hz, 2H), 7.60 (d, J=8.8 Hz, 2H), 7.44 (dd, J=15.6, 10.4 Hz, 1H), 7.05–6.91 (m, 2H), 6.11 (d, J=15.6 Hz, 1H), 4.25 (q, J=7.2 Hz, 2H), 1.33 ppm (t, J=7.2 Hz, 3H). The data were in agreement with the literature.[20]

(2*E*,4*E*)-5-Phenylpenta-2,4-dien-1-ol (9a):

Compound **9a** was synthesized from **8a** according to a literature procedure.[18] DIBAL-H (5.17 mL, 1.5 M in toluene) was added to a solution of **8a** (525 mg, 2.60 mmol) in CH_2Cl_2 (20 mL), the mixture was stirred at room temperature until no starting material remained (TLC plate checking). Then saturated potassium sodium tartrate tetrahydrate solution (20 mL) was added to the reaction mixture until the reaction mixture became clear. The resulting mixture was extracted with CH_2Cl_2 (20 mL) and EtOAc (20 mL×2). The organic layer was separated, dried with anhydrous $MgSO_4$, and concentrated in vacuum. The residue was purified by silica gel flash chromatography to give the title compound as a white solid (379 mg, 91%). R_f=0.47 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.39 (d, J=7.4 Hz, 2H), 7.31 (t, J=7.4 Hz, 2H), 7.22 (t, J=7.4 Hz, 1H), 6.78 (dd, J=15.6, 10.5 Hz, 1H), 6.55 (d, J=15.6 Hz, 1H), 6.41 (dd, J=15.1, 10.5 Hz, 1H), 5.99–5.91 (m, 1H), 4.23 (d, J=5.7 Hz, 2H), 1.71 ppm (br, 1H). The data were identical with those in the reference.[18]

Compounds **9b** and **9c** were synthesized using **8b** and **8c** as substrates according to the procedure given above for compound **9a**.

(2*E*,4*E*)-5-(4-Methoxyphenyl)penta-2,4-dien-1-ol (9b):

The title compound **9b** was prepared from **8b** (603 mg, 2.60 mmol) and DIBAL-H (5.17 mL, 1.5 M in toluene) as white solid (445 mg, 90%). R_f=0.39 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36 (d, J=8.8 Hz, 2H), 6.85 (d, J=8.8 Hz, 2H), 6.67 (dd, J=15.6, 10.4 Hz, 1H), 6.51 (d, J=15.6 Hz, 1H), 6.40 (dd, J=15.2, 10.4 Hz, 1H), 5.95–5.88 (m, 1H), 4.24 (d, J=6.0 Hz, 2H), 3.81 ppm (s, 3H). The data were in agreement with the literature.[21]

(2*E*,4*E*)-5-(4-Nitrophenyl)penta-2,4-dien-1-ol (9c):

The title compound **9c** was prepared from **8c** (642 mg, 2.60 mmol) and DIBAL-H (5.17 mL, 1.5 M in toluene) as a white solid (469 mg, 88%). R_f=0.45 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.18 (d, J=8.8 Hz, 2H), 7.52 (d, J=8.8 Hz, 2H), 6.94 (dd, J=15.6, 11.8 Hz, 1H), 6.60 (d, J=15.6 Hz, 1H), 6.48 (dd, J=15.2, 11.8 Hz, 1H), 6.14–6.08 (m, 1H), 4.31 ppm (d, J=4.4 Hz, 2H). The data were in agreement with the literature.[20]

(2*E*,4*E*)-5-Phenylpenta-2,4-dienal (4a):

Compound **4a** was synthesized from **9a** by following a literature procedure.[18] Dess–Martin periodinane (933 mg, 2.20 mmol) was added to a solution of **9a** (288 mg, 1.80 mmol) in CH_2Cl_2 (20 mL) and the mixture was stirred at room temperature until no starting material remained (TLC plate checking). The solvent was removed under vacuum. The residue was purified by silica-gel flash chromatography to give the title compound as a light yellow liquid (213 mg, 75%). R_f=0.76 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.62 (d, J=8.0 Hz, 1H), 7.53–7.49 (m, 2H), 7.41–7.35 (m, 3H), 7.27 (ddd, J=15.2, 7.2, 3.0 Hz, 1H), 7.02–7.00 (m, 2H), 6.28 ppm (dd, J=15.2, 8.0 Hz, 1H). The data were in agreement with the literature.[18]

Compounds **4b** and **4c** were synthesized using **9b** and **9c** as substrates, respectively, according to the procedure given above for compound **4a**.

(2*E*,4*E*)-5-(4-Methoxyphenyl)penta-2,4-dienal (4b):

The title compound **4b** was prepared from **9b** (342 mg, 1.80 mmol) and Dess–Martin periodinane (933 mg, 2.20 mmol) as white solid (247 mg, 73%). $R_f = 0.62$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.60$ (d, $J = 8.0$ Hz, 1H), 7.48–7.44 (m, 2H), 7.25 (dd, $J = 15.2$, 10.4 Hz, 1H), 7.00–6.85 (m, 4H), 6.23 (dd, $J = 14.8$, 8.0 Hz, 1H), 3.85 ppm (s, 3H). The data were in agreement with the literature.[22]

(2*E*,4*E*)-5-(4-Nitrophenyl)penta-2,4-dienal (4c):

The title compound **4c** was prepared from **9c** (369 mg, 1.80 mmol) and Dess–Martin periodinane (933 mg, 2.20 mmol) as white solid (300 mg, 82%). $R_f = 0.71$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.68$ (d, $J = 8.0$ Hz, 1H), 8.25–8.23 (d, $J = 8.8$ Hz, 2H), 7.65 (d, $J = 8.8$ Hz, 2H), 7.32–7.25 (m, 1H), 7.17–7.04 (m, 2H), 6.36 ppm (dd, $J = 8.0$, 7.2 Hz, 1H). The data were in agreement with the literature.[23]

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Keywords: dyes/pigments · fluorescence · single crystal analysis · solid-state luminescence · tunable emission color

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