

One-Step Stereoselective Synthesis of (2Z,4Z,6Z,8Z)-Decatetraene Diketone from Pyrylium Salts

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A strategy for the stereoselective synthesis of (2Z,4Z,6Z,8Z)decatetraene diketone by the one-step metal reduction of pyrylium salts is described. Reduction of α -active pyrylium salts (at least one H at the α -C positon) leads to only linear decatetraene diketone derivatives, whereas reduction of α -nonactive pyrylium salts (no H at the α -C position) generates two unexpected structures and one linear decatetraene diketone.

Introduction

Conjugated polyenes are basic skeletons in a variety of natural products such as isotretinoin,^[1,2] pheromones,^[3,4] and carotenoids.^[5-8] Recently, these compounds have attached growing interest as a result of their unique electronic structures and optoelectronic properties.^[9-11] Considerable efforts have been devoted to the development of synthetic approaches to polyene derivatives.^[12-14] Traditional methods are based on Wittig and Horner-Emmons-Wadsworth conversions^[15,16] and transition-metal-(especially Pd)-catalyzed cross-coupling reactions.[17-19] However, these methods often need multistep procedures or expensive catalysts, and the products are usually not totally chemo- and stereoselective.^[20] Recently, Takahashi et al. reported the regioselective formation of trienes and tetraenes from different alkynes by using a Zr/Cr or Zr/Cu system.^[21,22] Wu et al. explored the nickel-catalyzed tetramerization of alkynes to construct conjugated tetraenes.^[23] Xi and co-workers synthesized all-cis octatetraenes by dimerization of 1,4-dicopper-1,3-butadienes and subsequent Pd-catalyzed cross-coupling.^[24] In this context, it is desired to develop new, facile, and efficient methods for the stereoselective synthesis of conjugated polyenes.

Ring opening of cyclic and heterocyclic compounds provides an effective approach to linear π -conjugated systems.^[25,26] As a class of important intermediates, pyrylium

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The reaction conditions were optimized, and a reaction mechanism was proposed. Single-crystal structures of decatetraene diketone derivatives demonstrate the twisted configuration of the backbones and the all-(Z) geometry of the double bonds. In addition, the thermal, optical, and electrochemical properties of these compounds were studied in detail.

salts have been widely used in synthesizing carbocyclic and heterocyclic compounds through ring transformations.^[27–30] In contrast, ring-opening reactions of pyrylium salts have been rarely studied. For example, Balaban et al. and Marvell et al.^[31,32] independently reported that 2.4.6-trialkylpyrylium salts could be converted into dienones upon treatment with sodium borohydride. In our continuing research on the synthesis, optical properties, and reactivity of pyrylium salts,^[33-36] we became interested in constructing decatetraene diketone derivatives by dimerization of pyrylium salts. In this paper, we report a facile and efficient strategy for the stereoselective synthesis of decatetraene diketone derivatives by metal reduction of α -active and α -non-active pyrylium salts. By following this strategy, a series of (2Z, 4Z, 6Z, 8Z)-decatetraene-1, 10-diketone compounds were stereoselectively synthesized. A reaction mechanism was proposed, and crystal structures were investigated. Furthermore, the thermal, optical, and electrochemical properties of these compounds were studied.

Results and Discussion

Metal Reduction of α-Active Pyrylium Salts

In previous work, metal reduction of 2,4,6-triarylpyrylium salts (α -non-active) was shown to produce pyran γ -radicals at the C4 site, which led to pyran-4,4'-dimers.^[37–39] However, researchers speculated that this result deviated from the nature of pyran radicals. It is believed that pyran α -radicals (at the C2/C6 sites) can be obtained by changing the reaction conditions. In our previous report,^[33] α -active pyrylium salts were efficiently prepared from triarylcyclopentadienes. Compared to α -non-active pyrylium salts, α active pyrylium salts have lower steric hindrance and unique reactivity at the C2/C6 sites. Encouraged by these

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discoveries, the metal reduction reactions of α -active 2,4,5triarylpyrylium salts were investigated. As illustrated in Table 1, a series of linear π -conjugated decatetraene diketone derivatives were obtained in good yields.

Table 1. Synthesis of decatetraene diketone derivatives from α active pyrylium salts.

$\begin{array}{c} R^{3} \\ R^{4} \\ H \\ O_{+} \\ ClO_{4}^{-} \\ 1 \mathbf{a} - \mathbf{g} \end{array} \xrightarrow{Mg / CH_{3}CN} O \xrightarrow{R^{2}} R^{3} H \\ O \\ R^{1} R^{4} \\ H \\ R^{3} \\ R^{2} \\ R^{2} \\ R^{3} \\ R^{4} \\ H \\ R^{3} \\ R^{2} \\ \mathbf{a} - \mathbf{g} \end{array}$							
Entry	1	R ¹	R ²	R ³	R ⁴	2: Yield [%]	
1	1a	Ph	Н	Ph	Ph	2a : 83.3	
2	1b	$4-FC_6H_4$	Η	Ph	Ph	2b : 80.4	
3	1c	$4-BrC_6H_4$	Н	Ph	Ph	2c : 81.2	
4	1d	2-naphthyl	Н	Ph	Ph	2d : 85.4	
5	1e	$4-PhC_6H_4$	Н	Ph	Ph	2e : 84.8	
6	1f	Ph	Н	$4-PhC_6H_4$	$4-PhC_6H_4$	2f : 86.0	
7	1g	Ph	Ph	Ph	Ph	2g : 80.6	

To achieve optimum reaction conditions, the effects of reductant, solvent, and atmosphere were explored. Because of the poor stability of pyrylium salts in water and their poor solvability in nonpolar solvents, THF and CH₃CN were selected to dissolve the pyrylium salts. Taking **1a** as an example, the reaction details are summarized in Table 2. First, the reducing capacity of Mg, Zn, Fe, and Al was evaluated in CH₃CN. The yield of polyene diketone was the highest in Mg/CH₃CN. However, no conversion from the pyrylium salt into the decatetraene diketone was detected upon using Al as the reductant, probably because of the generation of a shielding film on the metal particles. Second, the reaction in Mg/THF was finished in a comparatively longer time and lower yield than the one in Mg/ CH₃CN because of the higher boiling point of CH₃CN. Third, an inert atmosphere such as Ar₂ was necessary, because the absence of oxygen could avoid the partial quenching of the intermediate pyran radical. As a result, the optimum reaction conditions for the synthesis of decatetraene diketones 2a-g involved the use of Mg as the metal, acetonitrile as the solvent, and Ar2 as an inert atmosphere with a reaction time of about 5 h. A possible reaction mechanism is proposed in Scheme 1. The decatetraene diketones were obtained by double Claisen rearrangement of pyran-6,6'dimers, which were generated by pyran α -radicals from α active pyrylium salts.

Entry	Reductant	M:1a	Solvent	Time [h]	2a:Yield [%]
1	Mg	50:1	CH ₃ CN	4	83.3
2	Zn	50:1	CH ₃ CN	5	70.8
3	Al	50:1	CH ₃ CN	12	_
4	Fe	50:1	CH ₃ CN	8	52.3
5	Mg	50:1	THF	6	77.6



Scheme 1. Proposed mechanism for metal reduction reactions of 1a-g.

Metal Reduction of α-Non-Active Pyrylium Salts

To examine the universality of this synthetic route, reduction reactions of three types of α -non-active pyrylium salts 3a-c under the similar conditions were performed. As shown in Table 3, only reduction of 3c generated (2Z,4E,6E,8Z)-decatetraene diketone 6. Products 4 and 5 without decatetraene chains were obtained and purified by recrystallization in methanol. The characterization results imply that a radical centered at C6 on the pyrylium cations was generated, which led to the fabrication of the pyran dimers. In comparison with the results we previously reported,^[34] the yields of the reduction reactions of 3a-c increased in the CH₃CN/Mg system. According to the results of the reduction reactions of the α -active and α -non-active pyrylium salts, we can draw the following conclusions: (1) Pyran α -radicals can be generated in THF or CH₃CN. (2) The reduction reactions reach high yields in the CH₃CN/Mg system. (3) The reduction of α -active pyrylium salts leads to linear decatetraene diketone structures; however, reduction of α -non-active pyrylium salts generates two other compounds without the all-(E)-decatetraene chains. As shown in Scheme 2, the mechanism of formation of 4

Table 3. Synthesis of polyene diketone derivatives from α -nonactive pyrylium salts.



5

Mg

Mg

1

2

3

3c

CH₃CN

6: 83.1

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Scheme 2. Proposed mechanism for metal reduction reactions of 3a and 3b.

and **5** is speculated to occur through dimerization of pyran α -radicals, which is followed by complicated transformations including Claisen rearrangement and Diels–Alder addition. The proposed mechanism implies that there is potential for the large-scale synthesis of pyran α -radicals by metal reduction of pyrylium cations. The mechanism for the reduction of **3c** is similar to that of **1a–g** (Scheme 1).

Crystal Structures of Decatetraene Diketones

To investigate the spatial structures and the relations between structures and properties, single crystals of decatetraene diketones **2a–c**, **2e**, and **2f** were prepared for X-ray diffraction experiment by vaporizing mixed solvents of CH_2Cl_2/CH_3OH at room temperature. The crystal data and structure refinements are tabulated in Table 4. Selected bond lengths and angles for these compounds are listed in Table S2 (Supporting Information).

The molecular structures of 2a-c, 2e, and 2f and their packing arrangements are shown in Figures 1, 2, 3, 4, and 5. As shown in the ORTEP drawings in Figures 1–5, the double bonds in these compounds have all-(Z) geometry. Another noteworthy feature of these molecules in the crys-

Table 4. Crystallographic data and structure refinement for 2a-c, 2e, and 2f.

	2a	2b	2c	2e	2f
Empirical formula	C ₄₆ H ₃₄ O ₂	C46H32F2O2	$C_{46}H_{32}Br_2O_2$	C ₅₉ H ₄₄ Cl ₂ O ₂	C ₇₀ H ₅₀ O ₂
Formula weight	618.73	654.72	776.54	855.84	923.10
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2/n	$P\overline{1}$	$P2_1/c$	$P\overline{1}$	C2/c
a [Å]	12.969(4)	8.5673(11)	9.630(8)	10.4943(5)	28.8673(7)
<i>b</i> [Å]	8.948(2)	12.0055(18)	22.534(18)	10.8997(5)	11.6645(2)
c [Å]	15.068(4)	18.147(2)	8.563(7)	21.0623(10)	18.6634(4)
Volume [Å ³]	1745.1(8)	1757.1(4)	1857(3)	2284.39(19)	5020.52(18)
Z	2	2	2	2	4
$D_{\rm calcd}$ [mg m ⁻³]	1.178	1.237	1.389	1.244	1.221
$\mu [\mathrm{mm}^{-1}]$	0.071	0.082	2.220	0.186	0.072
F(000)	652	684	788	896	1944
R _{int}	0.0471	0.0297	0.0502	0.0262	0.0409
GOF on F^2	1.014	0.990	1.005	1.051	1.257
$R_1 \left[I > 2\sigma(I)\right]^{[a]}$	0.0544	0.0674	0.0639	0.0661	0.0806
$wR_2 [I > 2\sigma(I)]^{[a]}$	0.1289	0.1863	0.1620	0.1831	0.2143
$R_1(all data)^{[a]}$	0.1306	0.1450	0.1755	0.1012	0.1317
wR_2 (all data) ^[a]	0.1625	0.2362	0.2065	0.2091	0.2430

[a] $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$; $wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)]^2 \}^{1/2}$.

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Figure 1. (a) ORTEP drawing of 2a with 30% probability thermal ellipsoids. (b) Schematic C-H··· π hydrogen-bonding interactions; the interaction distance and the angle of the C-H··· π center for I are 2.93 Å and 154°, respectively, and for II these values are 3.54 Å and 136°, respectively. (c) Stacking images of 2a.



Figure 2. (a) ORTEP drawing of **2b** with 30% probability thermal ellipsoids. (b) Schematic C–H··· π hydrogen-bonding interactions; the interaction distance and the angle of the C–H··· π center for I are 3.10 Å and 152°, respectively; for II these values are 3.07 Å and 149°, respectively; for III these values are 2.99 Å and 144°, respectively; for IV these values are 3.07 Å and 149°, respectively; and for V these values are 2.69 Å and 172°, respectively. (c) Stacking images of **2b**.



Figure 3. (a) ORTEP drawing of 2c with 30% probability thermal ellipsoids. (b) Schematic C–H··· π hydrogen-bonds interactions. The interaction distance and the angle of the C–H··· π center for I are 2.84 Å and 145°, respectively; for II these values are 2.83 Å and 146°, respectively; for III these values are 3.60 Å and 125°, respectively; and for IV these values are 2.73 Å and 161°, respectively. (c) Stacking images of 2c.

tal is torsion conformation, which is due to the large steric hindrance of the aryl groups linking to the double bonds. For example, the decatetraene chains of these compounds are not linear but have the twisted "S" configuration. As shown in Table 5, the torsion angles between double bonds and adjacent carbonyl [$\theta_{(0,1,2,3)}$] groups are distributed from 41 to 50°, and the torsion angle between the double bonds with the two adjacent aryl rings [$\theta_{(2,3,4,5)}$ and $\theta_{(6,7,8,9)}$] are in the 27–42° and 16–89° range, respectively. $\theta_{(4,3,7,8)}$ is clearly larger, from 64 to 74°. Intra- and intermolecular interactions and the molecular packing arrangements in the crystals are also shown in Figures 1–5. Although these molecules are packed into different crystal systems with different space groups, the stacking images are very similar, except for different intra- and intermolecular interactions. The molecules are packed into molecular layers on the basis of C– H··· π interactions. The twisted configuration and large steric hindrance make the π - π interaction impossible. The origin of non-fluorescence and low fluorescence efficiency of these compounds in solution and in the solid state are related to such a twisted configuration and the corresponding motion of the aryl groups linked to the single bond. The optical properties of these compounds will be discussed in the following section.



Figure 4. (a) ORTEP drawing of 2e with 30% probability thermal ellipsoids. (b) Schematic C–H··· π hydrogen-bonding interactions. The interaction distance and the angle of the C–H··· π center for I are 3.10 Å and 142°, respectively; for II these values are 3.41 Å and 117°, respectively; for III these values are 2.88 Å and 158°, respectively; for IV these values are 3.17 Å and 152°, respectively; and for V these values are 3.03 Å and 156°, respectively. (c) Stacking images of 2e.



Figure 5. (a) ORTEP drawing of **2f** with 30% probability thermal ellipsoids. (b) Schematic C–H··· π hydrogen-bonding interactions in **2f**. The interaction distance and the angle of the C–H··· π center for **I** are 3.22 Å and 137°, respectively; and for **II** these values are 3.36 Å and 156°, respectively. (c) Stacking images of **2f**.

Table 5. Selected torsion angles in 2a-c, 2e, and 2f.



Thermal, Optical, and Electrochemical Properties

The thermal properties of decatetraene diketone derivatives **2a–g** and **6** were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC curves were recorded during the second heating runs at a scan rate of 10 °C min⁻¹. As shown in Figure S3 and Table 6, **2d**, **2f**, **2g**, and **6** exhibit a glass transition peak, and the glass transition temperatures (T_g) are 80, 85, 82 and 81 °C, respectively. The decomposition temperature (T_d) is defined as the temperature at which 5% weight loss occurs during heating under a N₂ atmosphere. As shown in Table 6 and Figure S4, the compounds are stable, as they start to decompose at 240–320 °C. By comparing the values of T_d for these compounds, the introduction of bulky aryl groups and an increase in the quantity of aryl groups increase the thermal stability of this class of compounds.

The optical properties of **2a**–g and **6** in CH₂Cl₂ (5× 10^{-5} M) were investigated by UV/Vis absorption spectroscopy (UV) and photoluminescence (PL) spectroscopy. The maximum absorption wavelengths (λ_{abs}^{max}) were in the range from 301 to 381 nm (Figure 6 and Table 6), which was caused by π – π transitions. Compared to **2a**–g, the clear redshift of λ_{abs}^{max} for **6** to 381 nm is indicative of a more planar configuration in **6**. In dilute solution, these compounds barely exhibit emissions because of the vibration and rotation of the abundant single bonds, isomerization of the double bonds, and the twisted configuration of the

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Compound	Т _g [°С]	<i>T</i> _d [°C]	λ_{abs}^{max} [nm]	λ _{em} [nm]	${\Delta E_{ m g}}^{ m opt}$ [eV]	E _{HOMO} [eV]	E _{LUMO} [eV]
2a	_	257	311	465	2.54	-5.43	-2.89
2b	_	266	310	409	2.53	-5.37	-2.84
2c	_	267	309	476	2.56	-5.43	-2.87
2d	85	308	301	590	2.58	-5.47	-2.89
2e	_	290	308	547	2.57	-5.47	-2.90
2f	82	320	337	549	2.50	-5.45	-2.95
2g	80	240	324	527	2.63	-5.56	-2.93
6	81	280	381	437	2.66	-5.58	-2.92

Table 6. Thermal, optical properties, and energy levels of decatetraene diketones.

backbones, but the normalized PL spectra in Figure 7 illustrate the tunable emission properties of these compounds. As expected, no or very weak fluorescent emission was observed in solid powders and in the crystals because of the twisted configuration.



Figure 6. The normalized UV/Vis absorption spectra of decate traene ketones in CH_2Cl_2 .



Figure 7. The normalized PL spectra of decate traene ketones in $\rm CH_2Cl_2.$

It is well known that the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the energy band gaps (ΔE_g) are three important parameters for organic semiconductor materials.^[40] On the basis of cyclic voltammetry (CV) and the UV spectra, the HOMO levels and the values of ΔE_g were obtained by using the onset oxidation potential obtained from the CV curves (Figure S5) and the onset wavelength of UV absorp-

tion, respectively. As shown in Table 6, the $\Delta E_{\rm g}$ values of the compounds were in the 2.50–2.66 eV range and the HOMO values ranged from -5.37 to -5.58 eV.

Conclusions

In summary, a strategy for the stereoselective synthesis of (2Z,4Z,6Z,8Z)-decatetraene diketone through the onestep metal reduction of pyrylium salts was developed. Reduction of α -active pyrylium salts led only to linear decatetraene diketone derivatives, whereas reduction of α -nonactive pyrylium salts led to decatetraene diketone derivatives as well as other cyclic compounds. The crystal structures of these decatetraene diketones confirmed the twisted configuration of the backbones and the all-(Z) geometry of the double bonds. The predictability, stereoselectivity, and high yields illustrate the potential applications of this reaction. Moreover, the reaction conditions were optimized, and a reaction mechanism was proposed. Further studies are expanded to other heterocyclic salts to fabricate functional conjugated polyenes by metal reduction reactions.

Experimental Section

General Methods: All solvents were distilled before use unless otherwise stated. THF was distilled from sodium/benzophenone, and CH₃CN was distilled from P₂O₅ under a nitrogen atmosphere. ¹H NMR and ¹³C NMR spectra were recorded at 400 and 100.6 MHz, respectively. Mass spectra and high-resolution mass spectra (HRMS) were measured with a UPLC/Q-Tof. UV and fluorescence spectra were measured in 1 cm cells in CH₂Cl₂. DSC curves and TGA were obtained at a heating rate of 10 °Cmin⁻¹ under an atmosphere of N₂. Cyclic voltammetry (CV) measurements were performed in a three-electrode cell with a Pt disk working electrode, a Ag/AgNO₃ reference electrode, and a glassy carbon counter electrode. All CV measurements were performed under an atmosphere of N₂ with supporting electrolyte of 0.01 M tetra-*n*-butylammonium hexafluorophosphate in CH₃CN at a scan rate of 100 mV s⁻¹ by using ferrocene (Fc) as a standard.

Single-Crystal X-ray Crystallography: The X-ray diffraction data were collected at 100 K by using graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL. All non-hydrogen atoms were refined anisotropically.

CCDC-957385 (for **2a**), -957386 (for **2b**), -957387 (for **2c**), -957388 (for **2e**), -957389 (for **2f**), -957383 (for **5**), and -957384 (for **6**) con-

tain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthetic Procedure for Pyrylium Perchlorates: Pyrylium perchlorates 1a–g and 3c were synthesized according to our published method.^[33,36] A mixture of the cyclopentadiene derivatives (0.62 mmol) and perchloric acid (70%, 1 mL) in toluene/acetonitrile (3:1, 15 mL) was stirred at room temperature for 3 d. Diethyl ether (30 mL) was poured into the mixture. Then, the precipitate was obtained by filtration and washed with diethyl ether (3×15 mL). The crude product was recrystallized from acetic acid for purification. Pyrylium perchlorates 3a and 3b were synthesized according to the published procedure.^[41]

General Procedures for Metal Reduction of Pyrylium Salts: A 100 mL flask was charged with pyrylium perchlorate (1 mmol), Mg (50 mmol), and anhydrous CH₃CN (30 mL). The mixture was heated at reflux for 4–6 h under an atmosphere of Ar₂ and then cooled to room temperature. Magnesium and the magnesium salt were removed by filtration and washed with CH₂Cl₂ (3×30 mL). The crude product was obtained after the solvent was removed under reduced pressure. Purification was performed by recrystallization from methanol or flash column chromatography (silica gel, CH₂Cl₂/*n*-hexane). The crystals were prepared in CH₂Cl₂/CH₃OH.

(2*Z*,4*Z*,6*Z*,8*Z*)-1,3,4,7,8,10-Hexaphenyldecatetraene-1,10-dione (2a): Compound 1a (0.41 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield 2a (0.26 g, 0.42 mmol, 88.3%) as a yellow amorphous solid (silica gel, CH₂Cl₂/hexane = 1:1). ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (d, *J* = 6.8 Hz, 4 H), 7.52 (s, 2 H), 7.47 (t, *J* = 8.0 Hz, 2 H), 7.40 (m, 8 H), 7.30 (m, 6 H), 7.08 (s, 10 H), 6.84 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 190.8, 151.7, 141.6, 138.0, 132.8, 129.5, 128.8, 128.5, 128.5, 128.3, 128.2, 127.4, 126.7, 125.7, 125.4 ppm. HRMS: (ESI-TOF): calcd. for C₄₆H₃₄O₂Na [M + Na]⁺ 641.2457; found 641.2473. C₄₆H₃₄O₂ (618.77): calcd. C 89.29, H 5.54; found C 89.44, H 5.20.

(2*Z*,4*Z*,6*Z*,8*Z*)-1,10-Di(4-flourophenyl)-3,4,7,8-tetraphenyldecatetraene-1,10-dione (2b): Compound 1b (0.43 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield 2b (0.26 g, 0.40 mmol, 80.4%) as a yellow amorphous solid (recrystallization from methanol twice). ¹H NMR (400 MHz, CDCl₃): δ = 7.96–7.92 (m, 4 H), 7.44 (m, 6 H), 7.34 (m, 6 H), 7.10–7.00 (m, 14 H), 6.80 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 189.4, 151.8, 141.6, 139.4, 134.5, 134.5, 131.1, 131.0, 130.4, 129.7, 129.2, 128.9, 128.2, 127.4, 126.6, 125.6, 125.4, 115.6, 115.4 ppm. HRMS (ESI-TOF): calcd. for C₄₆H₃₂O₂F₂Na [M + Na]⁺ 677.2268; found 677.2313. C₄₆H₃₂F₂O₂ (654.75): calcd. C 84.38, H 4.93; found C 84.44, H 4.90.

(2*Z*,4*Z*,6*Z*,8*Z*)-1,10-Di(4-bromophenyl)-3,4,7,8-tetraphenyl decatetraene-1,10-dione (2c): Compound 1c (0.49 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield 2c (0.32 g, 0.41 mmol, 81.2%) as a yellow amorphous solid (silica gel, CH₂Cl₂/hexane = 1:1). ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, *J* = 8.4 Hz,4 H), 7.48–7.35 (m, 16 H), 7.11–7.06 (m, 10 H), 6.77 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 189.8, 152.28, 141.6, 1394, 136.9, 131.7, 130.0, 129.8, 128.9, 128.3, 127.7, 127.4, 126.6, 125.6, 125.1 ppm. HRMS (ESI-TOF): calcd. for C₄₆H₃₂O₂Br₂Na [M + Na]⁺ 797.0667; found 797.0670. C₄₆H₃₂Br₂O₂ (776.57): calcd. C 71.15, H 4.15; found C 71.19, H 4.23.

1,10-Di(2-naphthyl)-3,4,7,8-tetraphenyldecatetraene-1,10-dione (2d): Compound **1d** (0.46 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield **2d** (0.31 g, 0.43 mmol, 85.4%) as a yellow amorphous solid (silica gel, CH_2Cl_2 /hexane = 2:1). ¹H NMR



(400 MHz, CDCl₃): δ = 8.52 (s, 2 H), 8.04 (d, *J* = 8.0 Hz,2 H), 7.82 (m, 7 H), 7.64 (s, 2 H), 7.56 (m, 2 H), 7.50 (m, 2 H), 7.39 (d, *J* = 6.8 Hz,4 H), 7.27 (m, 4 H), 7.02 (d, *J* = 7.2 Hz,4 H), 6.95 (d, *J* = 7.2 Hz, 2 H), 6.88 (m, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 190.9, 151.3, 141.7, 139.4, 138.8, 135.6, 135.4, 132.5, 130.4, 129.5, 129.4, 128.8, 128.5, 128.4, 128.1, 127.8, 127.4, 126.8, 126.7, 126.2, 125.6, 124.2 ppm. HRMS (ESI-TOF): calcd. for C₅₄H₃₈O₂Na [M + Na]⁺ 741.2770; found 741.2744. C₅₄H₃₈O₂ (718.89): calcd. C 90.22, H 5.33; found C 90.19, H 5.39.

(2*Z*,4*Z*,6*Z*,8*Z*)-1,10-Di(4,4'-biphenyl)-3,4,7,8-tetraphenyldecatetraene-1,10-dione (2e): Compound 1e (0.48 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield 2e (0.33 g, 0.42 mmol, 84.8%) as a yellow amorphous solid (silica gel, CH₂Cl₂/hexane = 1:1). ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, *J* = 8.0 Hz, 4 H), 7.79 (d, *J* = 8.4 Hz,2 H), 7.70–7.67 (m, 2 H), 7.53 (d, *J* = 8.4 Hz,4 H), 7.48 (d, *J* = 8.0 Hz,6 H), 7.45 (s, 2 H), 7.42–7.36 (m, 8 H) 7.11– 7.02 (m 12 H), 6.78 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 190.5, 151.5, 145.5, 141.6, 140.0, 136.9, 130.5, 129.5, 129.1, 128.9, 128.5, 128.4, 128.2, 128.1, 127.8, 127.4, 127.279, 127.1, 126.7, 125.8, 125.7 ppm. HRMS (ESI-TOF): calcd. for C₅₈H₄₂O₂Na [M + Na]⁺ 793.3083; found 793.3043. C₅₈H₄₂O₂ (770.97): calcd. C 90.36, H 5.49; found C 90.42, H 5.56.

(2*Z*,4*Z*,6*Z*,8*Z*)-1,10-Diphenyl-3,4,7,8-tetra(4,4'-biphenylyl)decatetraene-1,10-dione (2f): Compound 1f (0.56 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield 2f (0.40 g, 0.43 mmol, 86.0%) as a yellow amorphous solid (recrystallization from methanol twice). ¹H NMR (400 MHz, CDCl₃): δ = 8.05 (d, *J* = 7.6 Hz,4 H), 7.67 (s, 2 H), 7.59–7.55 (m,12 H), 7.49–7.27 (m, 30 H), 7.00 (s, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 190.7, 151.3, 142.5, 140.7, 140.3, 140.2, 138.2, 133.0, 131.1, 129.8, 129.0, 128.9, 128.700, 128.6, 128.4, 127.9, 127.7, 127.3, 127.2, 127.1, 127.1, 127.0, 126.9, 126.7 ppm. HRMS (ESI-TOF): calcd. for C₇₀H₅₀O₂Na [M + Na]⁺ 945.3709; found 945.3743. C₇₀H₅₀O₂ (923.16): calcd. C 91.07, H 5.46; found C 91.15, H 5.56.

1,2,3,4,7,8,9,10-Octaphenyldecatetraene-1,10-dione (2g): Compound 1g (0.48 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield 2g (0.31 g, 0.40 mmol, 80.6%) as a yellow amorphous solid (2× recrystallization from methanol). ¹H NMR (400 MHz, CDCl₃): δ = 8.01 (d, *J* = 6.8 Hz, 2 H), 7.91 (d, *J* = 7.2 Hz, 2 H), 7.44 (t, *J* = 7.6 Hz, 1 H), 7.33 (m, 6 H), 7.1–6.9 (m, 26 H), 6.75 (d, *J* = 6.4 Hz, 4 H), 6.51 (d, *J* = 11.6 Hz, 1 H), 6.35 (d, 11.6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 197. 6, 196.6, 147.5, 146.4, 143.9, 142.5, 140.8, 139.3, 139.0, 138.3, 138.2, 137.8, 137.6, 137.0, 132.8, 132.7, 131.2, 130.6, 130.4, 130.2, 130.1, 130.0, 129.9, 128.4, 128.2, 127.8, 127.7, 127.5, 127.4, 127.3, 127.2, 127.1 ppm. HRMS (ESI-TOF): calcd. for C₅₈H₄₂O₂ (770.97): calcd. C 90.36, H 5.49; found C 90.27, H 5.64.

Dimer Derivate of 2,4,6-Tetraphenylpyrylium Salts (4): Compound **3a** (0.41 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield **4** (0.14 g, 0.23 mmol, 45.8%) as a yellow amorphous solid (2× recrystallization from methanol). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.68$ (d, J = 7.6 Hz, 2 H), 7.57 (d, J = 7.6 Hz, 2 H), 7.40 (d, J = 7.2 Hz, 2 H), 7.34 (m, 4 H), 7.19–7.13 (m, 4 H), 7.06–7.00 (m, 6 H), 6.87–6.72 (m, 8 H), 6.74 (d, J = 7.2 Hz, 2 H), 6.54 (s, 1 H), 5.55 (s, 1 H), 5.15 (d, J = 10 Hz, 1 H), 4.56 (d, J = 9.6 Hz, 1 H), 4.03 (d, J = 17.2 Hz, 1 H), 2.87 (d, J = 17.2 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 204.1$, 201.74 (s), 142.9, 140.4, 139.6, 139.2, 138.1, 137.8, 133.1, 132.4, 132.0, 131.7, 129.0, 128.7, 128.6, 128.3, 128.3, 128.2, 128.1, 128.0, 127.7, 127.5, 127.3, 127.2, 127.0, 126.5, 55.7, 49.7, 44.9, 37.2 ppm. MS (API-ES): m/z = 621.3 [M +

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1]⁺. C₄₆H₃₆O₂ (620.79): calcd. C 89.00, H 5.85; found C 89.16, H 5.94.

Dimer-Derivate of 2,3,4,6-Tetraphenylpyrylium Salts (5): Compound **3b** (0.48 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield **5** (0.21 g, 0.28 mmol, 55.1%) as a yellow amorphous solid (2× recrystallization from methanol). ¹H NMR (400 MHz, CDCl₃): δ = 7.52 (d, J = 7.6 Hz, 2 H), 7.46 (m, 2 H), 7.26 (m, 18 H), 6.90 (m, 8 H), 6.81 (t, J = 8.0 Hz, 3 H), 6.72 (t, J = 8.0 Hz, 3 H), 6.59 (d, J = 7.6 Hz, 2 H), 6.05 (d, J = 8.0 Hz, 2 H), 4.97 (s, 1 H), 4.36 (s, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 198.2, 148.1, 147.4, 147.1, 143.3, 142.2, 140.4, 140.0, 139.5, 138.1, 137.1, 136.92 (s), 134.9, 131.9, 131.2, 130.2, 129.6, 1328.3, 128.0, 127.6, 127.3, 127.1, 126.8, 126.6, 126.3, 126.0, 87.5, 83.4, 68.5, 58.2 ppm. MS (API-ES): m/z = 771.3 [M + 1]⁺. C₅₈H₄₂O₂ (770.97): calcd. C 90.36, H 5.49; found C 90.45, H 5.44.

(2*Z*,4*E*,6*E*,8*Z*)-Decaphenyldecatetraene-1,10-dione (6): Compound 3c (0.56 g, 1 mmol) was treated with Mg (1.2 g, 50 mmol) to yield 6 (0.38 g, 0.42 mmol, 83.1%) as a yellow amorphous solid (silica gel, CH₂Cl₂/hexane = 1:1). ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (d, *J* = 7.6 Hz, 10 H) 7.30–7.20 (m, 30 H), 7.16 (m, 10 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 197.6, 149.3, 145.6, 145.0, 143.2, 142.5, 142.0, 141.0, 138.0, 136.2, 131.4, 130.7, 129.6, 129.6, 128.0, 127.4, 127.3, 127.2, 126.7, 126.6, 126.4, 126.0, 125.9, 125.6 ppm. HRMS (ESI-TOF): calcd. for C₇₀H₅₀O₂Na [M + Na]⁺ 945.3709; found 945.3748. C₇₀H₅₀O₂ (923.16): calcd. C 91.07, H 5.46; found C 91.27, H 5.54.

Supporting Information (see footnote on the first page of this article): Copies of the ¹H NMR and ¹³C NMR spectra, MS and HRMS spectra, DSC curves, TGA curves, and CV curves, and X-ray crystallographic data.

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