

# Synthesis of Alkyl- and Alkoxy-Substituted Benzils and Oxidative Coupling to Tetraalkoxyphenanthrene-9,10-diones

Bernhard Mohr, Volker Enkelmann, and Gerhard Wegner\*

Max-Planck-Institut für Polymerforschung, Postfach 3148, LOFI 55021 Mainz, Germany

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Intermolecular Friedel–Crafts acylation of various substituted alkyl- or alkoxybenzenes with oxalyl chloride using carbon disulfide as solvent gave rise to the benzils 1a–k. Subsequent intramolecular oxidative coupling with either thallium(III) oxide/trifluoroacetic acid or vanadium(V) oxyfluoride/boron trifluoride diethyl etherate resulted in the corresponding phenanthrene-9,10-diones 2a–d. It has been shown that oxygen functionalities at the 3, 3', 4, and 4' positions are necessary for coupling to occur. These substituted benzils and phenanthrene-9,10-diones constitute precursors for ligands in the field of discotic metallomesogens or polymeric mesogens.

Alkyl- and alkoxy-substituted benzils constitute precursors for important classes of ligands, e.g. dioximes, dithiolenes, etc., in the field of discotic metallomesogens or polymeric mesogens.<sup>1</sup> Until now they have been prepared by a benzoin,<sup>2</sup> benzil,<sup>3</sup> or acyloin<sup>4</sup> condensation. These methods, however, are tedious and the overall yields are low. We now report a facile synthetic route to substituted benzils. Furthermore, we succeeded in the synthesis of the corresponding alkoxy-substituted phenanthrene-9,10-diones by oxidative coupling, a reaction until now believed to be impossible in the presence of benzylic oxygen atoms.<sup>5</sup> The formation of aromatic  $\alpha$ -diketo compounds through either inter-<sup>6</sup> or intramolecular<sup>7</sup> Friedel–Crafts reaction with oxalyl chloride is limited to only a few examples. Apparently, success in this reaction is strongly curtailed by the distinct tendency of oxalyl chloride to form [COCl<sub>2</sub>] or [COCl] which subsequently substitutes hydrogen atoms (aliphatic or aromatic) by chlorocarbonylation.<sup>8</sup> Chlorocarbonylation is especially favored under free radical conditions and in chlorinated solvents, such as trichloroethylene or dichloromethane. Neubart and Fishel reported the reaction of alkylbenzenes with oxalyl chloride and AlCl<sub>3</sub> under these conditions, resulting in 4-alkylbenzoyl chlorides in yields up to 80%, depending on the length of the alkyl substituent.<sup>9</sup>

We have now accomplished the conversion of several alkyl- and alkoxy-substituted benzenes to benzils in an intermolecular Friedel–Crafts acylation with oxalyl chlo-

ride, using CS<sub>2</sub> as solvent (Scheme 1). A wide variety of different substituted benzenes undergo this reaction. Results of these experiments are summarized in Table 1. The yields show a significant dependence on the nature and length of the attached substituents. For alkoxy-substituted derivatives, best results were accomplished with long or branched chains, while the methoxy derivative (entry 6) gave quite low yields. In the latter case, it is assumed that the decreased solubility of the intermediate Friedel–Crafts complex is responsible for this behavior. Notably, we found that conversion of the 1,3- and 1,4-dialkoxy-substituted benzenes furnished 2,2'-dihydroxy-4,4'-dialkoxy- and 2,2'-dihydroxy-5,5'-dialkoxy-substituted benzils, respectively (entries 10 and 11). Thus ethers in position *ortho* to the carbonyl functionalities are selectively cleaved, presumably favored by the formation of hydrogen bonds which are formed between the hydroxy and the carbonyl groups in the products.<sup>11,12</sup> This is confirmed not only by the fact that the carbonyl groups are coplanar with the hydroxy groups in the X-ray crystal structure<sup>13</sup> of 2,2'-dihydroxy-4,4'-bis(octyloxy)benzil (Figure 1) but also by the fact that cleavage is not observed when the starting materials are exposed to either AlCl<sub>3</sub> or oxalyl chloride in CS<sub>2</sub> separately. The hydrogen-bond lengths in the crystal amount to 1.72(1) Å and 1.82(1) Å, with O–H–O angles of 128.5(5)° and 128.0(5)°, respectively. Both carbonyl groups are coplanar with the adjacent phenyl ring, the phenyl rings are twisted by 85.4(1)°.

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(1) For reviews, see: (a) Giroud-Godquin, A.-M.; Maitlis, P. M. *Angew. Chem.* 1991, 103, 370; *Angew. Chem., Int. Ed. Engl.* 1991, 30, 375. (b) Bruce, D. W. in *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley: Chichester, 1992. (c) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Solo, E. *Coord. Chem. Rev.* 1992, 117, 215.

(2) Wenz, G. *Makromol. Chem., Rapid Commun.* 1985, 6, 577.

(3) (a) Ohta, K.; Takagi, A.; Muroki, H.; Yamamoto, I.; Matsuzaki, K.; Inabe, T.; Maruyama, Y. *J. Chem. Soc., Chem. Commun.* 1986, 883. (b) Ohta, K.; Takagi, A.; Muroki, H.; Yamamoto, I.; Matsuzaki, K. *Mol. Cryst. Liq. Cryst.* 1987, 147, 15.

(4) Ohta, K.; Hasabe, H.; Ema, H.; Mori, M.; Fujimoto, T.; Yamamoto, I. *Mol. Cryst. Liq. Cryst.* 1991, 208, 21.

(5) (a) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem.* 1990, 102, 1006; *Angew. Chem., Int. Ed. Engl.* 1990, 29, 977. (b) Magnus, P.; Schultz, J.; Gallagher, T. *J. Am. Chem. Soc.* 1985, 107, 4984. (c) Magnus, P.; Schultz, J.; Gallagher, T. *J. Chem. Soc., Chem. Commun.* 1984, 1179.

(6) Tüchtin, C.; Ogliaruso, M.; Becker, E. I. *Org. Synth.* 1961, 41, 1.

(7) (a) Trost, B. M. *J. Am. Chem. Soc.* 1969, 91, 918. (b) Sangaiah, R.; Gold, A. *J. Org. Chem.* 1987, 52, 3205.

(8) Neubart, M. E.; Fishel, D. L. *Mol. Cryst. Liq. Cryst.* 1979, 53, 101.

(9) Neubart, M. E.; Fishel, D. L. *Org. Synth.* 1983, 61, 8.

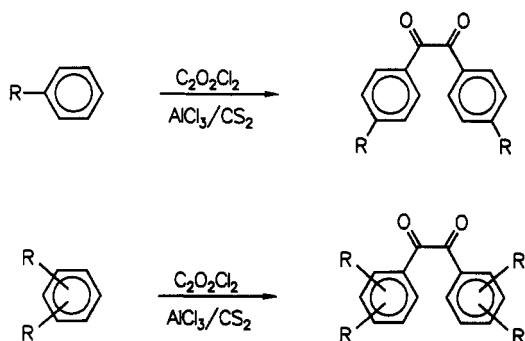
(10) Complete workup of the reaction mixture yielded also 32% diocetylbenzophenone, 21% 4-octylbenzoyl chloride, 6% educt, and 9% unidentified products.

(11) We also made the identical observation in an intramolecular Friedel–Crafts acylation of 2,7-dialkoxy-3,6-dialkylacenaphthenes. Conversion with oxalyl chloride resulted in 3,8-dihydroxy-4,7-dialkylacenaphthene-1,2-diones.

(12) <sup>1</sup>H NMR spectroscopy for the compound 1j shows a sharp singlet for the bridging hydrogen atom at  $\delta = 11.8$  ppm (CDCl<sub>3</sub>, TMS).

(13) The crystallographic data collection was carried out on a Nonius CAD4 diffractometer with graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.5405$  Å). Intensities were determined with the  $\theta$ - $2\theta$  scan mode to a limiting scattering angle  $\theta_{\max} = 55^\circ$ . Structures were solved by direct methods (SIR) and refined by full-matrix least-squares analyses with anisotropic temperature factors for C and O. Compound 1j crystallizes in the triclinic space group *P*-1 with  $a = 5.1753(10)$  Å,  $b = 13.5798(8)$  Å,  $c = 20.9742(8)$  Å,  $\alpha = 102.072(4)^\circ$ ,  $\beta = 93.124(8)^\circ$ ,  $\gamma = 99.709(10)^\circ$ ,  $V = 1414.6$  Å<sup>3</sup>,  $D_x = 1.17$  g/cm<sup>3</sup>, and  $Z = 2$ . Final least-squares refinement using 2115 unique reflections with  $I > 3\sigma(I)$  gave  $R$  ( $R_w$ ) = 0.053 (0.059). Compound 2c crystallizes in the monoclinic space group *C2/c* with  $a = 35.4695(17)$  Å,  $b = 9.8609(4)$  Å,  $c = 10.4396(19)$  Å,  $\beta = 99.981(10)^\circ$ ,  $V = 3596.1$  Å<sup>3</sup>,  $D_x = 1.22$  g/cm<sup>3</sup>, and  $Z = 4$ . Final least-squares refinement using 1774 unique reflections with  $I > 3\sigma(I)$  gave  $R$  ( $R_w$ ) = 0.052 (0.049). The authors have deposited atomic coordinates for these compounds with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Scheme 1



Oxidative biaryl coupling reactions with oxidants like thallium(III) oxide, vanadium(V) oxyfluoride, and other transition-metal oxides have been developed as a powerful tool for intramolecular coupling, often used for the synthesis of various alkaloids.<sup>14,15</sup> Studies by Halton and co-workers have shown that oxygen functionalities *meta* and *para* to the coupling position are essential for cyclization to occur.<sup>16</sup> The attractiveness of this oxidation approach appeared to be restricted by the inability to carry out this reaction in the presence of a benzoyl group. We were pleased to succeed in the conversion of 3,3',4,4'-tetraalkoxy-substituted benzils to the corresponding phenanthrene-9,10-diones through oxidative coupling with either thallium(III) oxide or vanadium(V) oxyfluoride, as depicted in Scheme 2. Attempts to accomplish coupling with 4,4'-dialkoxy-substituted and 2,2',4,4'- or 2,2',5,5'-tetraalkoxy-substituted benzils, or with alkyl-substituted benzils, failed. Table 2 summarizes the results of these experiments. Excellent yields are obtained using vanadium(V) oxyfluoride as oxidant (entries 12–16), whereas oxidation with thallium(III) oxide (entry 17) gave significantly lower yields. Attempts with palladium(II) acetate as oxidant (entry 18) were unsuccessful. Figure 2 depicts the molecular crystal structure of 2,3,6,7-tetrakis(hexyloxy)phenanthrene-9,10-dione.<sup>13</sup> The diones **2a–d** were further converted to the corresponding dioximato and dithiolato metal complexes.<sup>17</sup>

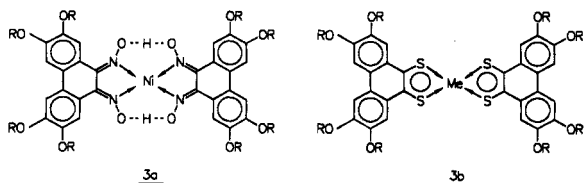
In summary, we have achieved convenient access to a variety of alkyl- and alkoxy-substituted benzils via intermolecular Friedel–Crafts reaction. Yields depend strongly on the nature of the substituents and we have not yet

(14) (a) For a good review see ref 5a. (b) Landais, Y.; Lebrun, A.; Lenain, V.; Robin, J. P. *Tetrahedron Lett.* 1987, 28, 5161. (c) Landais, Y.; Rambault, D.; Robin, J. P. *Ibid.* 1987, 28, 543. (d) Sawyer, J. S.; Macdonald, T. L. *Tetrahedron* 1988, 29, 4839. (e) Cambie, R. C.; Clark, G. R.; Craw, P. A.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* 1984, 37, 1775.

(15) For reductive coupling of benzils to phenanthrene-9,10-diones with  $C_8K$ , see: (a) Tamarkin, D.; Rabinovitz, M. *J. Org. Chem.* 1987, 52, 3474. (b) Tamarkin, D.; Benny, D.; Rabinovitz, M. *Angew. Chem.* 1984, 96, 594; *Angew. Chem., Int. Ed. Engl.* 1984, 23, 642.

(16) Halton, B.; Maidment, A. I.; Officer, D. L.; Warnes, J. M. *Aust. J. Chem.* 1984, 37, 2119.

(17) Conversion of the compounds **2a–d** with (1)  $NH_2OH \cdot HCl$  and (2)  $Ni(ac)_2$  gave bis(tetraalkoxyphenanthrene-9,10-dione dioximato)Ni(II) (**3a**); conversion with (1)  $P_2S_5$  and (2)  $NiCl_2$  yielded bis(tetraalkoxyphenanthrene-9,10-dithiolato)Ni(II) (**3b**). These mesogenic complexes the subject of future publications.

Table 1. Conversion of Various Substituted Benzenes via Friedel–Crafts Acylation with Oxalyl Chloride<sup>a</sup>

entry	substrate	product	com- pound	% isolated yield
1			1a	32 <sup>10</sup>
2			1b	34
3			1c	44
4			1d	42
5			1e	37
6			1f	1.7
7			1g	45
8			1h	24
9			1i	41
10			1j	23
11			1k	17

<sup>a</sup> See text for standard reaction conditions. <sup>b</sup> Based on the substituted benzenes as the limiting reagent.

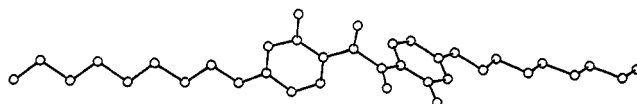
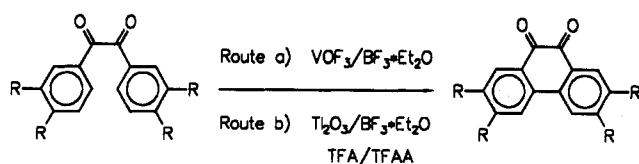


Figure 1. Molecular crystal structure of 2,2'-dihydroxy-4,4'-diocetyloxybenzil.

optimized the reaction conditions for each case. The simplicity of this reaction relative to known procedures has much promise for further development, although this

Scheme 2

Table 2. Intramolecular Oxidative Coupling of 3,3',4,4'-Tetrakis(alkoxy)-Substituted Benzils (Scheme 2)<sup>a</sup>

entry	substituent	reagent/solvent	% isolated yield <sup>b</sup>	compd
12	R = OCH <sub>3</sub>	VOF <sub>3</sub> /CH <sub>2</sub> Cl <sub>2</sub>	23	2a
13	R = OCH <sub>3</sub>	VOF <sub>3</sub> /C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	88	2a
14	R = O-iC <sub>8</sub> H <sub>11</sub>	VOF <sub>3</sub> /CH <sub>2</sub> Cl <sub>2</sub>	82	2b
15	R = OC <sub>6</sub> H <sub>13</sub>	VOF <sub>3</sub> /CH <sub>2</sub> Cl <sub>2</sub>	86	2c
16	R = OC <sub>10</sub> H <sub>21</sub>	VOF <sub>3</sub> /CH <sub>2</sub> Cl <sub>2</sub>	91	2d
17	R = OC <sub>10</sub> H <sub>21</sub>	Ti <sub>2</sub> O <sub>3</sub> /CH <sub>2</sub> Cl <sub>2</sub>	36	2d
18	R = OC <sub>10</sub> H <sub>21</sub>	Pd(ac) <sub>2</sub> /AcOH	0 <sup>c</sup>	

<sup>a</sup> See text for standard reaction conditions. <sup>b</sup> Based on the substituted benzils as the limiting reagent. <sup>c</sup> Only substrate recovered.

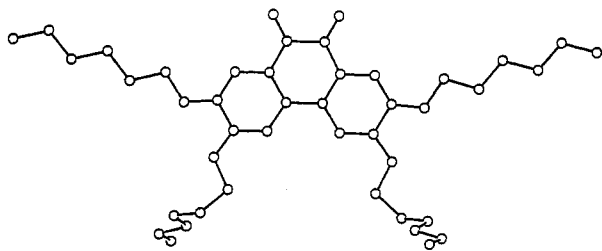


Figure 2. Molecular crystal structure of 2,3,6,7-tetrahexyloxyphenanthrene-9,10-dione.

reaction afforded modest yields of the desired product. 3,3',4,4'-Tetraalkoxy-substituted benzils were converted to phenanthrene-9,10-diones by intramolecular oxidative coupling in high yields.

## Experimental Section

**General Procedures.** NMR spectra were recorded on a Bruker AX-300 using CDCl<sub>3</sub> as solvent and internal standard. Mass spectra were measured on a VG ZAB2-SE-FPD. Elemental analyses were carried out at the University of Mainz. Melting points were determined with a Mettler DSC TC 11. Thin-layer chromatography was performed using Merck F-60 TLC plates. Column chromatography was performed on silica gel (230–400 mesh, Merck).

**General Procedure for the Synthesis of Dialkoxy-Substituted Benzenes.** A mixture of 27.5 g (250 mmol) of dihydroxybenzene, 600 mmol of alkyl bromide, and 103.7 g (750 mmol) of powdered potassium carbonate was stirred in 600 mL of DMF for 9 h at 80 °C under argon. Upon cooling to room temperature, 500 mL of water was added and the organic layer was separated. The aqueous layer was extracted with 1 L of ether and the combined organic layers were washed with water, dried (MgSO<sub>4</sub>), and then evaporated to dryness to yield an off-white solid. Final purification was achieved through recrystallization from ethanol.

**General Procedure for the Synthesis of 1,2-Dialkyl-Substituted Benzenes.** *n*-Alkylmagnesium bromide (2.5 equiv) in ether was slowly added to an ice-cooled and stirred mixture of 117.6 g (800 mmol) of 1,2-dichlorobenzene and 500 mg (0.8 mmol) of Ni(dppp)Cl<sub>2</sub> in 600 mL of dry ether under argon. The mixture was then refluxed for 48 h and cooled to 0 °C, and the reaction was carefully quenched with 200 mL of water, followed by addition of 300 mL of 2 N HCl. After separation of the layers, the aqueous medium was extracted with ether and the combined organic layers were washed with water, dried (MgSO<sub>4</sub>), and concentrated *in vacuo*. Distillation through a Vigreux column under reduced pressure yielded the desired product as a viscous oil.

**General Procedure for the Synthesis of Alkyl- and Alkoxy-Substituted Benzils.** Solvents and glassware used in this synthesis were dried thoroughly prior to use. To a mechanically stirred suspension of 200 mmol of alkyl- or alkoxybenzene and 28.3 g (220 mmol) of aluminum chloride in 500 mL of carbon disulfide at 0 °C was added a solution of 15.2 g (120 mmol) of oxalyl chloride in 100 mL of carbon disulfide over a period of 4 h under a constant stream of argon. Stirring was continued for 18 h. The resulting brown mixture was poured onto 500 mL of ice and the yellow organic phase was separated. The aqueous medium was extracted with dichloromethane and the combined organic layers were washed with water, dried (MgSO<sub>4</sub>), and concentrated *in vacuo*. The resulting orange residue was chromatographed over a bed of silica gel to remove carboxylic acids and inorganic residues using dichloromethane as eluent. The obtained material was then recrystallized from ethanol or acetone. Final purification was achieved by column chromatography (silica gel) with dichloromethane as eluent.

**General Procedure for the Oxidative Coupling with Thallium(III) Oxide.** Alkoxy-substituted benzil (5 mmol) was added to a suspension of 1.4 g (3.0 mmol) of thallium(III) oxide in 50 mL of anhydrous dichloromethane containing 5 mL of trifluoroacetic acid and 5 mL of trifluoroacetic anhydride under argon. Then 1.49 g (10.5 mmol) of boron trifluoride etherate was added immediately, the resulting dark reaction mixture was stirred for 90 min at ambient temperature and poured into citric acid (10%, 50 mL), and the organic layer was separated. The aqueous layer was extracted with 50 mL of dichloromethane and the combined organic layers were washed with water, dried (MgSO<sub>4</sub>), and reduced *in vacuo*. The resulting dark residue was subjected to column chromatography (silica gel/dichloromethane) to provide a deep red solid.

**General Procedure for Oxidative Coupling with Vanadium(V) Oxyfluoride.** To a stirred solution of 5 mmol of alkyl- or alkoxy-substituted benzil and 1.49 g (10.5 mmol) of boron trifluoride etherate in 25 mL of anhydrous dichloromethane (compound 1f: 1,1,2,2-tetrachloroethane) was added 2.05 g (16.5 mmol) of vanadium(V) oxyfluoride. The reaction mixture was stirred for 30 min at ambient temperature and poured into citric acid (10%, 50 mL), and the organic layer was separated. The aqueous layer was extracted with 50 mL of dichloromethane and the combined organic layers were washed with water, dried (MgSO<sub>4</sub>), and reduced *in vacuo*. The resulting dark residue was subjected to column chromatography (silica gel/dichloromethane) to provide a deep red solid.

**4,4'-Dioctylbenzil (1a):** yellow oil (32%); <sup>1</sup>H NMR δ 7.87 (d, 2H, *J* = 8.36 Hz), 7.28 (d, 2H, *J* = 8.36 Hz), 2.65 (t, 2H, *J* = 7.70 Hz), 1.65–1.56 (m, 2H), 1.30–1.18 (m, 10H), 0.86 (t, 3H, *J* = 6.76 Hz); <sup>13</sup>C NMR δ 194.48, 150.93, 130.89, 130.03, 129.03, 36.20, 31.81, 29.36, 29.21, 29.17, 22.61, 14.04; FD *m/z* (relative intensity) 434 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>30</sub>H<sub>42</sub>O<sub>2</sub>: C, 82.90; H, 9.74. Found: C, 82.63; H, 9.76.

**4,4'-Dioctyloxybenzil (1b):** yellow oil (34%); <sup>1</sup>H NMR δ 7.89 (d, 2H, *J* = 8.36 Hz), 6.94 (d, 2H, *J* = 8.36 Hz), 4.03 (t, 2H, *J* = 6.67 Hz), 1.86–1.77 (m, 2H), 1.50–1.38 (m, 2H), 1.35–1.20 (m, 8H), 0.86 (t, 3H, *J* = 6.99 Hz); <sup>13</sup>C NMR δ 193.33, 164.34, 132.16, 126.00, 114.34, 69.29, 31.68, 29.20, 29.09, 28.94, 25.87, 22.52, 13.94; FD *m/z* (relative intensity) 466 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>30</sub>H<sub>42</sub>O<sub>4</sub>: C, 77.22; H, 9.07. Found: C, 77.01; H, 9.08.

**3,3',4,4'-Tetramethylbenzil (1c):** offwhite solid (44%); mp 124 °C; <sup>1</sup>H NMR δ 7.71 (d, 1H, *J* = 1.85 Hz), 7.66 (dd, 1H, *J* = 8.00, 1.85 Hz), 7.22 (d, 1H, *J* = 8.00 Hz), 2.31 (s, 3H), 2.28 (s, 3H); <sup>13</sup>C NMR δ 194.90, 144.77, 137.46, 131.04, 130.67, 130.16, 127.66, 20.18, 19.59; FD *m/z* (relative intensity) 266 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>: C, 81.18; H, 6.81. Found: C, 81.23; H, 6.84.

**3,3',4,4'-Tetrahexylbenzil (1d):** yellow oil (42%); <sup>1</sup>H NMR δ 7.78 (d, 1H, *J* = 1.83 Hz), 7.67 (dd, 1H, *J* = 7.99, 1.83 Hz), 7.22 (d, 1H, *J* = 7.99 Hz), 2.66 (t, 2H, *J* = 6.24 Hz), 2.63 (t, 2H, 6.28 Hz), 1.62–1.52 (m, 4H), 1.40–1.25 (m, 12H), 0.88 (t, 3H, *J* = 7.08 Hz), 0.87 (t, 3H, *J* = 6.92 Hz); <sup>13</sup>C NMR δ 194.88, 148.67, 141.55, 130.98, 130.32, 129.65, 127.68, 32.99, 32.55, 31.63, 30.95, 30.80, 29.31, 22.54, 14.00; FD *m/z* (relative intensity) 546 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>38</sub>H<sub>58</sub>O<sub>2</sub>: C, 83.46; H, 10.69. Found: C, 83.70; H, 10.73.

**3,3',4,4'-Tetradecylbenzil (1e):** white solid (37%); mp 41 °C; <sup>1</sup>H NMR δ 7.76 (d, 1H, *J* = 1.83 Hz), 7.65 (dd, 1H, *J* = 8.01,

1.83 Hz), 7.22 (d, 1H,  $J = 8.01$  Hz), 2.65 (t, 2H,  $J = 7.11$  Hz), 2.63 (t, 2H,  $J = 7.36$  Hz), 1.60–1.53 (m, 4H), 1.30–1.15 (m, 28H), 0.86 (t, 6H,  $J = 6.87$  Hz);  $^{13}\text{C}$  NMR  $\delta$  194.95, 148.76, 141.63, 131.03, 130.35, 129.68, 127.75, 33.04, 32.62, 31.92, 31.06, 30.88, 29.66, 29.48, 29.35, 22.69, 14.09; FD  $m/z$  (relative intensity) 771 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{54}\text{H}_{90}\text{O}_2$ : C, 84.09; H, 11.76. Found: C, 84.11; H, 11.79.

**3,3',4,4'-Tetramethoxybenzil (1f)**: white solid (1.7%); mp 260 °C;  $^1\text{H}$  NMR  $\delta$  7.58 (d, 1H,  $J = 1.95$  Hz), 7.46 (dd, 1H,  $J = 8.40, 1.95$  Hz), 6.87 (d, 1H,  $J = 8.40$  Hz), 3.94 (s, 3H), 3.93 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  193.43, 154.83, 149.56, 126.51, 126.24, 110.40, 110.35, 56.20, 56.08; FD  $m/z$  (relative intensity) 330 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_6$ : C, 65.45; H, 5.49. Found: C, 65.36; H, 5.63.

**3,3',4,4'-Tetrakis(isopentyloxy)benzil (1g)**: white solid (45%); mp 78 °C;  $^1\text{H}$  NMR  $\delta$  7.55 (d, 1H,  $J = 1.97$  Hz), 7.42 (dd, 1H,  $J = 8.36, 1.97$  Hz), 6.83 (d, 1H,  $J = 8.36$  Hz), 4.07 (t, 2H,  $J = 6.59$  Hz), 4.06 (t, 2H,  $J = 6.62$  Hz), 1.90–1.76 (m, 2H), 1.74–1.61 (m, 4H), 0.95 (d, 6H,  $J = 6.50$  Hz), 0.94 (d, 6H,  $J = 6.47$  Hz);  $^{13}\text{C}$  NMR  $\delta$  193.75, 155.01, 149.36, 126.25, 126.07, 112.35, 111.62, 67.72, 67.60, 37.79, 37.59, 25.18, 22.59, 22.54; FD  $m/z$  (relative intensity) 554 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{34}\text{H}_{50}\text{O}_6$ : C, 73.61; H, 9.08. Found: C, 73.69; H, 9.27.

**3,3',4,4'-Tetrakis(hexyloxy)benzil (1h)**: white solid (24%); mp 97 °C;  $^1\text{H}$  NMR  $\delta$  7.54 (d, 1H,  $J = 1.98$  Hz), 7.41 (dd, 1H,  $J = 8.48, 1.98$  Hz), 6.83 (d, 1H,  $J = 8.48$  Hz), 4.04 (t, 2H,  $J = 6.61$  Hz), 4.03 (t, 2H,  $J = 6.63$  Hz), 1.87–1.76 (m, 4H), 1.49–1.42 (m, 4H), 1.41–1.27 (m, 8H), 0.89 (t, 3H,  $J = 7.00$  Hz), 0.88 (t, 3H,  $J = 7.01$  Hz);  $^{13}\text{C}$  NMR  $\delta$  193.79, 155.01, 149.32, 126.24, 126.08, 112.42, 111.66, 69.27, 69.14, 31.49, 29.04, 28.90, 25.64, 25.58, 22.58, 22.55, 13.97; FD  $m/z$  (relative intensity) 614 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{38}\text{H}_{58}\text{O}_6$ : C, 74.72; H, 9.57. Found: C, 74.53; H, 9.76.

**3,3',4,4'-Tetrakis(decyloxy)benzil (1i)**: white solid (41%); mp 93 °C;  $^1\text{H}$  NMR  $\delta$  7.54 (d, 1H,  $J = 1.99$  Hz), 7.41 (dd, 1H,  $J = 8.48, 1.99$  Hz), 6.82 (d, 1H,  $J = 8.48$  Hz), 4.04 (t, 2H,  $J = 6.63$  Hz), 4.03 (t, 2H,  $J = 6.67$  Hz), 1.86–1.77 (m, 4H), 1.50–1.38 (m, 4H), 1.35–1.20 (m, 24H), 0.86 (t, 6H,  $J = 6.99$  Hz);  $^{13}\text{C}$  NMR  $\delta$  193.75, 155.01, 149.33, 126.25, 126.09, 112.43, 111.67, 69.29, 69.15, 31.91, 29.57, 29.34, 29.09, 28.94, 25.99, 25.92, 22.68, 14.09; FD  $m/z$  (relative intensity) 835 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{54}\text{H}_{90}\text{O}_6$ : C, 77.65; H, 10.86. Found: C, 77.62; H, 10.79.

**2,2'-Dihydroxy-4,4'-bis(octyloxy)benzil (1j)**: white solid (23%); mp 99 °C;  $^1\text{H}$  NMR  $\delta$  11.81 (s, 1H), 7.36 (d, 1H,  $J = 8.91$  Hz), 6.46 (d, 1H,  $J = 2.37$  Hz), 6.40 (dd, 1H,  $J = 8.91, 2.37$  Hz), 3.99 (t, 2H,  $J = 6.55$  Hz), 1.82–1.72 (m, 2H), 1.44–1.37 (m, 2H), 1.34–1.22 (m, 8H), 0.87 (t, 3H,  $J = 6.96$  Hz);  $^{13}\text{C}$  NMR  $\delta$  194.30, 167.23, 166.67, 133.85, 110.75, 109.03, 101.56, 68.62, 31.64, 29.11, 29.03, 28.75, 25.77, 22.49, 13.89; FD  $m/z$  (relative intensity) 498 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{30}\text{H}_{42}\text{O}_6$ : C, 72.26; H, 8.49. Found: C, 72.31; H, 8.61.

**2,2'-Dihydroxy-5,5'-bis(decyloxy)benzil (1k)**: white solid (17%); mp 104 °C;  $^1\text{H}$  NMR  $\delta$  11.79 (s, 1H), 7.37 (d, 1H,  $J = 8.87$  Hz), 6.46 (d, 1H,  $J = 2.41$  Hz), 6.40 (dd, 1H,  $J = 8.87, 2.41$  Hz), 3.98 (t, 2H,  $J = 6.59$  Hz), 1.81–1.72 (m, 2H), 1.44–1.36 (m, 2H), 1.34–1.19 (m, 12H), 0.87 (t, 3H,  $J = 6.91$  Hz);  $^{13}\text{C}$  NMR  $\delta$  194.36, 167.33, 166.81, 133.81, 110.68, 109.12, 101.55, 68.69, 31.81, 29.17, 29.08, 28.81, 25.83, 22.54, 13.90; FD  $m/z$  (relative intensity) 554 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{34}\text{H}_{50}\text{O}_6$ : C, 73.61; H, 9.08. Found: C, 73.31; H, 9.41.

**2,2',4,4'-Tetrakis(octyloxy)benzil (1l)**. A mixture of 1.0 g (2.0 mmol) of 1j, 1.0 g (5.2 mmol) of octyl bromide, and 0.83 g (6.0 mmol) of powdered potassium carbonate was stirred in 50 mL of DMF for 9 h at 70 °C under argon. Upon cooling to room temperature, 50 mL of water was added and the organic layer was separated. The aqueous layer was extracted with ether and

the combined organic layers were washed with water, dried ( $\text{MgSO}_4$ ), and then evaporated to dryness to yield an off-white oil. Recrystallization from 40 mL of methanol–acetone (1:1) at –20 °C yielded 0.90 g (72%) of a white solid:  $^1\text{H}$  NMR  $\delta$  8.01 (d, 1H,  $J = 8.73$  Hz), 6.54 (dd, 1H,  $J = 8.73, 2.16$  Hz), 6.33 (d, 1H,  $J = 2.16$  Hz), 3.97 (t, 2H,  $J = 6.58$  Hz), 3.78 (t, 2H,  $J = 6.14$  Hz), 1.81–1.73 (m, 2H), 1.46–1.41 (m, 2H), 1.40–1.18 (m, 20H), 0.88 (t, 3H,  $J = 7.01$  Hz), 0.87 (t, 3H,  $J = 6.96$  Hz);  $^{13}\text{C}$  NMR  $\delta$  191.89, 165.43, 161.74, 132.34, 116.89, 106.33, 98.82, 69.04, 68.38, 31.87, 31.78, 29.32, 29.19, 29.13, 28.53, 26.07, 25.96, 22.63, 14.08; FD  $m/z$  (relative intensity) 723 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{48}\text{H}_{74}\text{O}_6$ : C, 76.41; H, 10.31. Found: C, 76.21; H, 10.19.

**2,2',5,5'-Tetrakis(decyloxy)benzil (1m)** was obtained by reaction of 1k with decyl bromide as described for 1l: white solid (74%); mp 32 °C;  $^1\text{H}$  NMR  $\delta$  7.99 (d, 1H,  $J = 8.71$  Hz), 6.54 (dd, 1H,  $J = 8.71, 2.17$  Hz), 6.33 (d, 1H,  $J = 2.17$  Hz), 3.98 (t, 2H,  $J = 6.59$  Hz), 3.79 (t, 2H,  $J = 6.17$  Hz), 1.81–1.73 (m, 2H), 1.46–1.40 (m, 2H), 1.40–1.16 (m, 28H), 0.88 (t, 3H,  $J = 6.96$  Hz), 0.87 (t, 3H,  $J = 6.99$  Hz);  $^{13}\text{C}$  NMR  $\delta$  191.93, 165.48, 161.69, 132.39, 116.76, 106.30, 98.80, 69.12, 68.41, 31.83, 31.75, 29.34, 29.29, 29.15, 28.64, 26.15, 25.99, 22.61, 14.00; FD  $m/z$  (relative intensity) 835 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{54}\text{H}_{90}\text{O}_6$ : C, 77.65; H, 10.86. Found: C, 77.31; H, 10.61.

**2,3,6,7-Tetramethoxyphenanthrene-9,10-dione (2a)**: red solid (88%); mp 144 °C;  $^1\text{H}$  NMR  $\delta$  7.53 (s, 1H), 7.12 (s, 1H), 4.06 (s, 3H), 3.96 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  179.00, 155.55, 149.68, 131.13, 124.69, 111.67, 105.49, 56.23, 56.10; FD  $m/z$  (relative intensity) 328 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_6$ : C, 65.85; H, 4.91. Found: C, 65.71; H, 4.93.

**2,3,6,7-Tetrakis(isopropoxy)phenanthrene-9,10-dione (2b)**: red solid (82%); mp 143 °C;  $^1\text{H}$  NMR  $\delta$  7.34 (s, 1H), 6.95 (s, 1H), 4.17 (t, 2H,  $J = 6.53$  Hz), 4.00 (t, 2H, 6.72 Hz), 1.92–1.80 (m, 2H), 1.79–1.66 (m, 4H), 0.99 (d, 6H,  $J = 6.56$  Hz), 0.95 (d, 6H,  $J = 6.51$  Hz);  $^{13}\text{C}$  NMR  $\delta$  179.07, 155.21, 149.42, 131.01, 124.42, 112.90, 107.04, 67.91, 67.59, 37.77, 25.21, 22.60; FD  $m/z$  (relative intensity) 552 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{34}\text{H}_{48}\text{O}_6$ : C, 73.88; H, 8.75. Found: C, 73.56; H, 8.99.

**2,3,6,7-Tetrakis(hexyloxy)phenanthrene-9,10-dione (2c)**: red solid (86%); mp 87 °C;  $^1\text{H}$  NMR  $\delta$  7.43 (s, 1H), 7.03 (s, 1H), 4.15 (t, 2H,  $J = 6.46$  Hz), 4.01 (t, 2H,  $J = 6.63$  Hz), 1.89–1.78 (m, 4H), 1.39–1.31 (m, 12H), 0.90 (t, 3H,  $J = 6.99$  Hz), 0.89 (t, 3H,  $J = 7.05$  Hz);  $^{13}\text{C}$  NMR  $\delta$  179.16, 155.57, 149.45, 131.09, 124.46, 112.97, 107.19, 69.53, 69.11, 31.53, 29.08, 29.00, 25.65, 25.62, 22.56, 13.96; FD  $m/z$  (relative intensity) 608 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{38}\text{H}_{56}\text{O}_6$ : C, 74.96; H, 9.27. Found: C, 74.89; H, 9.44.

**2,3,6,7-Tetrakis(decyloxy)phenanthrene-9,10-dione (2d)**: red solid (91%); mp 88 °C;  $^1\text{H}$  NMR  $\delta$  7.41 (s, 1H), 7.00 (s, 1H), 4.15 (t, 2H,  $J = 6.44$  Hz), 4.00 (t, 2H,  $J = 6.65$  Hz), 1.91–1.76 (m, 4H), 1.56–1.25 (m, 28H), 0.86 (t, 6H,  $J = 6.71$  Hz);  $^{13}\text{C}$  NMR  $\delta$  179.13, 155.56, 149.42, 131.07, 124.42, 112.95, 107.16, 69.51, 69.09, 31.89, 29.59, 29.55, 29.38, 29.32, 29.13, 29.04, 26.00, 25.66, 22.65, 14.05; FD  $m/z$  (relative intensity) 833 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{54}\text{H}_{88}\text{O}_6$ : C, 77.84; H, 10.64. Found: C, 77.66; H, 10.43.

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**Supplementary Material Available:** Experimental procedures and spectral data (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.