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### Synthesis of a Nickel Bis(dithiolene) Complex with Strong Near-Infrared Two-Photon Absorption

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## Synthesis of a Nickel Bis(dithiolene) Complex with Strong Near-Infrared Two-Photon Absorption

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*The diketones 4,4'-di[3,4-bis(n-dodecyloxy)styryl]benzil and 4,4'-di[3,4-bis(n-dodecyloxy)phenylethynyl]benzil have been synthesized from 4,4'-dibromobenzil using Heck coupling with the appropriate styrene and Sonogashira coupling with the appropriate phenylalkyne, respectively. Treatment of the distyrylbenzil derivative with phosphorus pentasulfide followed by nickel(II) chloride gave the corresponding extended nickel bis(dithiolene) derivative which shows strong near-infrared two-photon absorption with a cross-section of over 440 GM (1 GM = 10<sup>-50</sup> cm<sup>4</sup> s photon<sup>-1</sup> molecule<sup>-1</sup>) throughout the telecommunications range and a peak cross-section of 5300 GM at ca. 1.2 μm.*

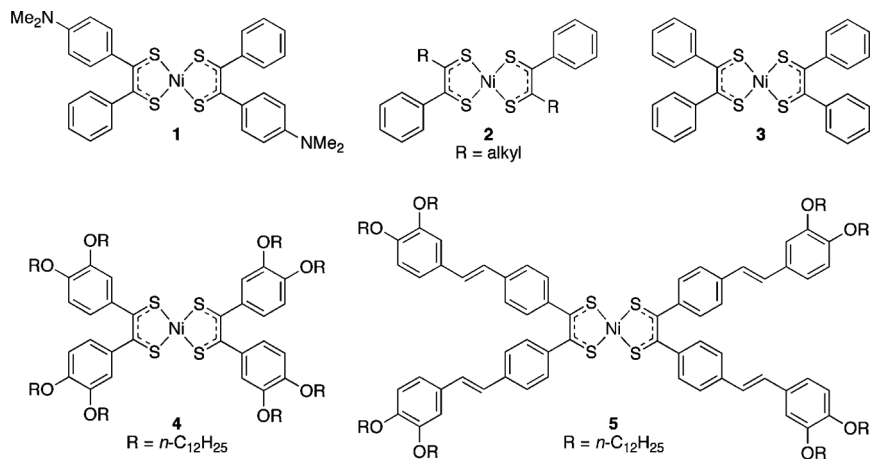
**Keywords:** dithiolene; nickel; two-photon absorption; Z-scan

## INTRODUCTION

The third-order nonlinear optical properties of bis(dithiolene) nickel complexes such as the dye known as BDN, **1**, and dyes of the general type **2** (Fig. 1) have attracted considerable interest [1–5]. Dyes of type

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**FIGURE 1** Structures of some nickel bis(dithiolene)s discussed in the text.

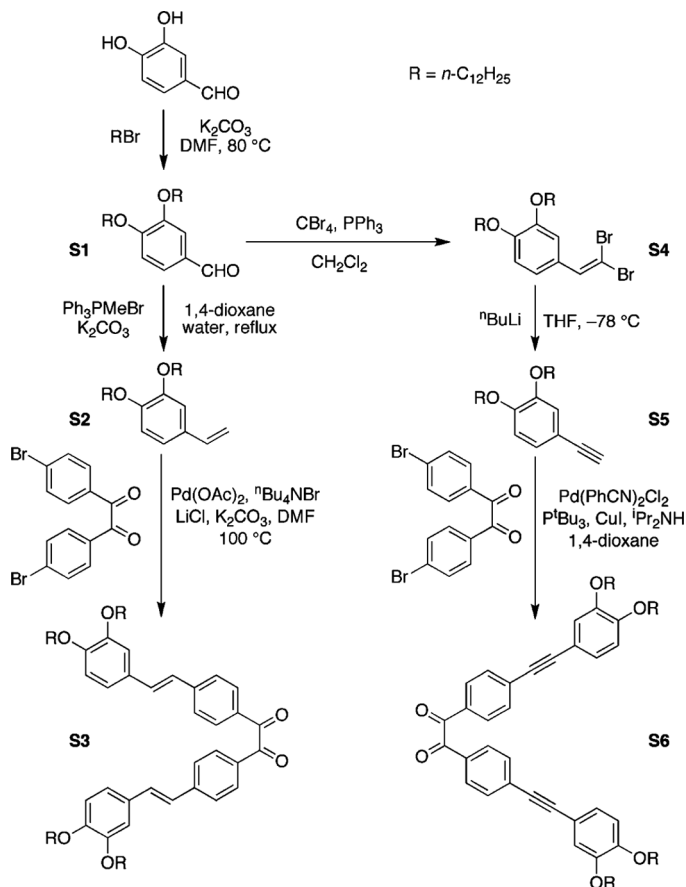
**2** were reported to have large values of the real parts of the third-order susceptibility,  $\text{Re}(\chi^3)$ , at  $1.06\ \mu\text{m}$ , suggesting potential applications in all-optical switching [3,4], although subsequent studies showed that these susceptibilities were not purely electronic in origin [5]. Only one study has addressed the two-photon absorption (2PA) properties of nickel bis(dithiolene)s; this study on films containing **2** was aimed at demonstrating that the real part of the susceptibility was large compared to the imaginary part at  $1.06\ \mu\text{m}$  [4,6], since  $\text{Im}(\chi^3)$ , to which 2PA is often a major contributor, is detrimental for all-optical switching, with  $\text{Re}(\chi^3)/\text{Im}(\chi^3)$  being a frequently used figure-of-merit for these applications [7].

More recently, 2PA has attracted attention as a useful phenomenon with potential applications for three-dimensional microfabrication, high-density memory, biological imaging, and photodynamic therapy [8], rather than merely as a nuisance detrimental to applications based on exploiting  $\text{Re}(\chi^3)$ .  $\pi$ -Conjugated chromophores with various structural motifs incorporating  $\pi$ -donors (D) and  $\pi$ -acceptors (A) have been shown to exhibit high peak 2PA cross-sections,  $\delta_{\text{max}}$ ; these include D-A-D [9–15], A-D-A [9,16–19], D-A [13,20–23], and multipolar systems [24–26]. Electrochemical measurements indicate that the nickel bis(dithiolene) moiety has a rather low-lying LUMO and these properties have been exploited in conducting and superconducting charge-transfer salts of the type  $[\text{X}]_x[\text{M}(\text{dmit})_2]$  {X = organic cation, dmit = 1,3-dithiol-2-thione-4,5-dithiolato} [27,28] and in the use of neutral nickel bis(dithiolene)s (such as **1** and **4**) in *n*-channel field-effect

transistors [29–31], suggesting they might also be used as acceptors in conjugated  $\pi$ -systems. Nickel bis(dithiolene)s generally exhibit rather low-energy one-photon absorption (1 PA) bands, suggesting that two-photon-allowed states may be sufficiently low-lying for 2 PA in the telecommunications region (1.3–1.55  $\mu\text{m}$ ) of the near-infrared (NIR), in which range only a few chromophores have been characterized [15,23,32,33] and where potential applications include optical pulse suppression [34], all-optical beam stabilization, dynamic-range compression, and the sensitization of photorefractive composites [35,36]. We have recently reported that nickel bis(dithiolene) complexes **3** [37], **4** [31,38,39], and **5** (Fig. 1) show increasingly strong NIR 2PA with a peak cross-section as high as 5300 GM (1 GM =  $10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ ) being observed for **5** [40]. In this article we describe the synthesis and characterization of the new chromophore **5** in more detail.

## RESULTS AND DISCUSSION

Figure 2 shows the synthetic route adopted for the synthesis of **5**, along with the synthesis of some other compounds undertaken in an unsuccessful attempt to obtain its alkyne-containing analogue, **6**. Intermediate **S1** was synthesized from the commercial 3,4-dihydroxybenzaldehyde essentially as described as in the literature [41]. During the course of our work, similar syntheses of **S2** [42] and **S4–S5** [43] have been published, although with only minimal characterization of these intermediates. For **S2**, both our synthesis and the recently reported synthesis rely on a Wittig reaction between **S1** and methyl triphenylphosphonium bromide; our synthesis is based on a general procedure involving potassium carbonate in wet 1,4-dioxane [44], while Gehringer and co-workers obtained a somewhat higher yield using more traditional conditions of potassium *tert*-butoxide in tetrahydrofuran [42]. We obtained the dibromovinyl derivative, **S4**, by treating **S1** with 1 equivalent of carbon tetrabromide and 2 equivalents of triphenylphosphine, following a procedure described for 4-(2,2-dibromovinyl)-1,2-dimethoxybenzene [45], while Gehringer and co-workers obtained similar yields using 5 equivalents each of carbon tetrabromide, triphenylphosphine, and zinc [43]. Treatment with strong base (*n*-butyl lithium in our case, lithium di-*iso*-propylamide in Gehringer's work [43]) leads to formation of the terminal alkyne, **S5**. The two diketone precursors, **S3** and **S6**, were obtained as yellow solids in good yield by coupling commercially available 4,4'-dibromobenzil with the terminal alkene or alkyne under Heck or Sonogashira conditions, respectively [46].



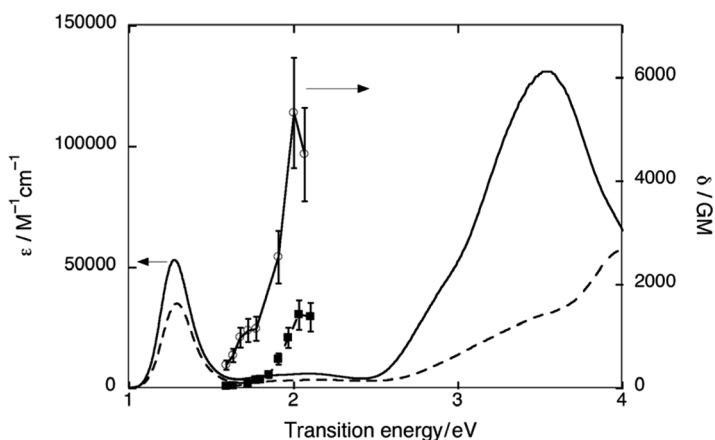
**FIGURE 2** Synthesis of new diketones with extended conjugation and alkoxy donors.

Nickel bis(dithiolene)s can be synthesized in a number of ways [47] including treatment of nickel(II) salts with dithiones, with solvent molecules presumably acting as *in situ* reducing agents; we adopted this approach, initially forming the dithiones *in situ* by treatment with phosphorus pentasulfide in 1,4-dioxane, and then adding aqueous nickel(II) chloride. The product **5** was isolated as a dark green solid in moderate yield after careful column chromatography. While we were unable to obtain satisfactory combustion analysis for **5**, despite repeated chromatography and attempts at crystallization, the identity of the compound was clearly established by NMR spectroscopy and mass spectrometry;  $^1\text{H}$  NMR spectroscopy suggested that there were

no (< 1%) conjugated impurities that could contribute to the observed nonlinear absorption (*vide infra*). Attempts to prepare **6** in the same way were unsuccessful; although the product showed the characteristic visible–NIR absorption spectrum of a nickel bis(dithiolene), with a low-energy maximum at 939 nm, a broad  $^1\text{H}$  NMR spectrum with few resolvable peaks and poor solubility are suggestive of formation of an oligomerized or polymerized material.

Figure 3 compares the one-photon visible–NIR spectrum of **5** with that of its analogue **4** which has a less extensive  $\pi$ -system. The characteristic near-IR absorption of nickel bis(dithiolene)s, which has been assigned to a  $\pi$ - $\pi^*$  absorption delocalized over the core of the complex [47], occurs at similar energy in the two complexes, corresponding to photon wavelengths of 960–970 nm. Weak absorptions in the 1.8–2.3 eV (550–700 nm) range, which have been assigned to d–d transitions [47], are also similar in the two complexes. The most significant difference between the spectra of **4** and **5** is in the strong UV absorption of the latter, corresponding to a photon wavelength of 350 nm and presumably due to transitions localized in the stilbene units of the ligands.

Figure 3 also shows degenerate 2PA spectra acquired using open-aperture Z-scan measurements [48,49]. Compounds **4** and **5** show similar 2PA profiles, with apparent maxima at state energies of *ca.* 2.0 eV (the error bars do not allow us to definitively rule out the possibility that the true maxima occur at slightly higher energy),



**FIGURE 3** One-photon (lines) and two-photon (lines and data points) spectra of **4** (broken lines, filled squares, data taken in chloroform) and **5** (solid lines, open circles, tetrahydrofuran).

corresponding to photon energies of *ca.* 1.0 eV and to photon wavelengths of *ca.* 1.2  $\mu\text{m}$ . However, the cross-sections differ significantly with peak cross-sections of 1400 and 5300 GM for **4** and **5** respectively. For **5**,  $\delta = 2500$  GM at the telecommunications wavelength of 1.3  $\mu\text{m}$  and  $\delta$  exceeds 440 GM throughout the entire telecommunications range. Figure 3 shows that 2PA-allowed state lies at very similar energy to the 1PA d-d states; however, the differences in 2PA spectra between **4** and **5** (and **3**) indicate that there must be considerable ligand contributions to the 2PA state. For centrosymmetric chromophores such as these complexes, 1PA states are 2PA-forbidden and vice versa; the cross-section for degenerate 2PA from the ground state,  $g$ , into an excited state,  $e'$ , is given by terms of form

$$\delta \propto E_{ge'}^2 \frac{\mu_{ge}^2 \mu_{ee'}^2}{(E_{ge} - (E_{ge'}/2))^2} \quad (1)$$

where the  $e$  subscript denotes an intermediate 1PA-allowed state and where  $E$  and  $\mu$  denote energies and transition dipole moments respectively. Thus, the small detuning energies,  $E_{ge} - (E_{ge'}/2)$ , of  $< 0.3$  eV between the virtual states and the intermediate 1PA states for **4** and **5** are important factors contributing to large  $\delta$ . However, consideration of the energy terms does not explain the *difference* in cross-section between **4** and **5**, which, according to Eq. (1), must be dominated by differences in the transition dipole moment terms [50]. One of these transition dipole moment terms,  $\mu_{ge}$ , can be determined from 1PA spectra using the relation

$$\mu_{ge} = 0.09584 \sqrt{\frac{\int \varepsilon(\bar{\nu}) d\bar{\nu}}{\bar{\nu}_{\max}}} \quad (2)$$

where  $\bar{\nu}_{\max}$  and  $\varepsilon(\bar{\nu})$  are in  $\text{cm}^{-1}$  and  $\text{M}^{-1} \text{cm}^2$  respectively. Values of 8.0 and 11.2 D are found for **4** and **5** respectively; this difference may arise from extension of the frontier orbitals, and, therefore, of the 1PA transition density, onto the styryl groups of the ligands of **5**. Using Eq. (1) one can see that these values of  $\mu_{ge}$  would be expected to lead to an increase of  $\delta_{\max}$  by a factor of *ca.* 2 between **4** and **5**, whereas the experimental values of  $\delta_{\max}$  differ by a factor of *ca.* 4. The transition dipole moments linking the 1PA and 2PA states,  $\mu_{ee'}$ , are less readily experimentally determined (although, in principle, accessible through pump-probe measurements). However, if one assumes the same detuning energies for **4** and **5**, and that a single three-level term with the low-energy 1PA state as an intermediate state dominates the 2PA response, the discrepancy between the ratios in the  $\mu_{ge}$  and  $\delta_{\max}$



suggests a ratio of ca. 1.4 between the values of  $\mu_{ee'}$  for **5** and **4**, presumably also due to more extensive delocalization of the  $e \rightarrow e'$  transition density in **5**.

## EXPERIMENTAL DETAILS

### 3,4-Bis(*n*-dodecyloxy)benzaldehyde (**S1**)

K<sub>2</sub>CO<sub>3</sub> (50.0 g, 0.362 mol) and 1-bromododecane (90.3 g, 0.362 mol) were added to a solution of 3,4-dihydroxybenzaldehyde (25.0 g, 0.181 mol) in DMF (400 mL). The reaction mixture was heated at 80°C for 45 h under N<sub>2</sub> atmosphere. Water was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and saturated aq. NaCl several times and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the product was further dried under vacuum overnight to give an off-white solid (52.8 g, 62%). mp 69–70°C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  9.80 (s, 1 H), 7.36–7.41 (m, 2 H), 6.92 (d,  $J$  = 8.6 Hz, 1 H), 4.03 (q,  $J$  = 6.2 Hz, 4 H), 1.81 (m, 4 H), 1.44 (m, 4 H), 1.24 (s, 32 H), 0.85 (t,  $J$  = 6.4 Hz, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  190.92, 154.65, 149.42, 129.85, 126.54, 111.72, 110.93, 69.08, 31.89, 29.58, 29.34, 29.04, 28.96, 25.92, 22.66, 14.07. IR (cm<sup>-1</sup>): 2916, 2847, 1686, 1672, 1584, 1506, 1277, 1236, 1133, 807, 800. HRMS (FAB) calcd for C<sub>31</sub>H<sub>55</sub>O<sub>3</sub> (MH<sup>+</sup>), 475.4151; found, 475.4156. Anal. Calcd for C<sub>31</sub>H<sub>54</sub>O<sub>3</sub>: C, 78.43; H, 11.46. Found: C, 78.46; H, 11.72.

### 3,4-Bis(*n*-dodecyloxy)styrene (**S2**)

A mixture of Ph<sub>3</sub>PMeBr (8.79 g, 24.6 mmol), K<sub>2</sub>CO<sub>3</sub> (3.4 g, 24.6 mmol), **S1** (10.0 g, 21.1 mmol), 1,4-dioxane (25 mL), and H<sub>2</sub>O (0.3 mL) was refluxed for 24 h, allowed to cool to room temperature, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extracts were washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, evaporated under reduced pressure, and purified by column chromatography (silica gel, 2:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) to give **S2** as a white solid (6.53 g, 66%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.96 (d,  $J$  = 1.9 Hz, 1 H), 6.90 (dd,  $J$  = 8.0 Hz, 1.9 Hz, 1 H), 6.80 (d,  $J$  = 8.2 Hz, 1 H), 6.62 (dd,  $J$  = 17.3 Hz, 10.7 Hz, 1 H), 5.57 (dd,  $J$  = 17.6 Hz, 0.5 Hz, 1 H), 5.11 (d,  $J$  = 11.5 Hz, 1 H), 3.98 (q,  $J$  = 6.6 Hz, 4 H), 1.74–1.85 (m, 4 H), 1.19–1.50 (m, 36 H), 0.87 (t,  $J$  = 6.6 Hz, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  149.01, 148.98, 136.44, 130.63, 119.46, 113.44, 111.50, 111.18, 69.24, 32.00, 29.78, 29.72, 29.51, 29.45, 29.38, 29.34, 26.12, 22.78, 14.22. HRMS(EI) calcd for C<sub>32</sub>H<sub>56</sub>O<sub>2</sub>, 472.4280; found, 472.4267. Anal. Calcd C<sub>32</sub>H<sub>56</sub>O<sub>2</sub>: C, 81.29; H, 11.94. Found: C, 81.36; H, 11.99.

### 4,4'-Di[3,4-bis(*n*-dodecyloxy)styryl]benzil (**S3**)

**S2** (5.78 g, 12.2 mmol), 4,4'-dibromobenzil (1.8 g, 4.9 mmol),  $K_2CO_3$  (3.38 g, 24.5 mmol),  $^nBu_4NBr$  (1.58 g, 4.9 mmol),  $LiCl$  (0.21 g, 4.9 mmol),  $Pd(OAc)_2$  (0.11 g, 0.49 mmol), and dry DMF (40 mL) were heated at 100°C under Ar for 60 h, allowed to cool to room temperature, and extracted with  $CH_2Cl_2$ . The organic extracts were washed with  $H_2O$ , dried over  $MgSO_4$ , evaporated under reduced pressure, and purified by column chromatography (silica gel, 1:2 to 3:2  $CH_2Cl_2$ /hexanes) and recrystallization from  $CH_2Cl_2$ /hexanes to give **S2** as a bright yellow solid (4.27 g, 76%).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.94 (d,  $J$  = 8.2 Hz, 2 H), 7.58 (d,  $J$  = 8.5 Hz, 2 H), 7.18 (d,  $J$  = 16.2 Hz, 2 H), 7.08 (d,  $J$  = 1.9 Hz, 2 H), 7.05 (dd,  $J$  = 8.2 Hz, 1.9 Hz, 2 H), 6.96 (d,  $J$  = 16.2 Hz, 2 H), 6.85 (d,  $J$  = 8.2 Hz, 2 H), 4.03 (t,  $J$  = 6.6 Hz, 4 H), 4.01 (t,  $J$  = 6.6 Hz, 4 H), 1.76–1.88 (m, 8 H), 1.20–1.53 (m, 72 H), 0.86 (t,  $J$  = 6.6 Hz, 12 H).  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  193.70, 149.87, 149.12, 144.09, 132.51, 131.28, 130.40, 129.32, 126.39, 124.83, 120.81, 113.29, 111.53, 69.37, 69.15, 32.00, 29.78, 29.73, 29.52, 29.46, 29.38, 29.29, 26.14, 26.11, 22.80, 14.24. MS(EI)  $m/z$  1152 ( $M^+$ ). Anal. Calcd for  $C_{78}H_{118}O_6$ : C, 81.34; H, 10.33. Found: C, 81.25; H, 10.35.

### Compound 5

**S3** (1.0 g, 0.87 mmol),  $P_2S_5$  (0.58 g, 1.3 mmol), and *p*-dioxane (20 mL) were refluxed for 5 h under  $N_2$ , allowed to cool to 60°C, and filtered under  $N_2$ .  $NiCl_2 \cdot 6H_2O$  (0.103 g, 0.43 mmol) in  $H_2O$  (1.5 mL) was added to the filtrate; the resulting mixture was refluxed overnight and then allowed to cool to room temperature, and extracted with  $CH_2Cl_2$ . The organic extracts were washed with  $H_2O$ , dried over anhydrous  $MgSO_4$  and evaporated under reduced pressure. The resulting dark green solid was washed with acetone and MeOH and purified by column chromatography (silica gel, 1:1 hexanes/ $CH_2Cl_2$ ) to give a dark green solid, **5** (0.314 g, 30%).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.39 (s, 16 H), 6.81–7.11 (m, 20 H), 4.02 (t,  $J$  = 6.9 Hz, 8 H), 3.99 (t,  $J$  = 6.9 Hz, 8 H), 1.75–1.88 (m, 16 H), 1.16–1.52 (m, 144 H), 0.864 (t,  $J$  = 6.6 Hz, 12 H), 0.861 (t,  $J$  = 6.6 Hz, 12 H).  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  180.73, 149.33, 149.13, 140.05, 138.22, 130.10, 129.76, 129.26, 126.16, 125.69, 120.26, 113.51, 111.43, 69.35, 69.21, 32.01, 29.79, 29.73, 29.54, 29.46, 29.35, 26.15, 22.78, 14.24. MS(MALDI)  $m/z$  2426 ( $M^+$ ).

### 4-(2,2-Dibromovinyl)-1,2-bis(*n*-dodecyloxy)benzene (**S4**)

To a well-stirred solution of  $CBr_4$  (6.99 g, 21.1 mmol) in dry  $CH_2Cl_2$  at 0°C was added  $PPh_3$  (11.05 g, 42.1 mmol) and **S1** (10.0 g, 21.1 mmol).

The resulting mixture was stirred for 1 h at ambient temperature. The reaction mixture solidified during the time. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$ , washed with  $\text{H}_2\text{O}$ , and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure to give an off-white solid. The product was further purified by column chromatography (silica gel, 2:1 hexanes/ $\text{CH}_2\text{Cl}_2$ ) to give a yellowish white solid (11.37 g, 86%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (s, 1 H), 7.17 (d,  $J = 2.2$  Hz, 1 H), 7.04 (dd,  $J = 8.5$  Hz, 0.6 Hz, 1 H), 6.82 (d,  $J = 8.5$  Hz, 1 H), 3.983 (t,  $J = 6.6$  Hz, 2 H), 3.976 (t,  $J = 6.9$  Hz, 2 H), 1.75–1.85 (m, 4 H), 1.20–1.50 (m, 36 H), 0.87 (t,  $J = 6.6$  Hz, 6 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  149.37, 148.37, 136.38, 127.67, 121.85, 113.51, 112.72, 86.90, 69.29, 69.00, 32.00, 29.78, 29.70, 29.51, 29.45, 29.26, 26.09, 22.78, 14.24. HRMS(EI) calcd for  $\text{C}_{32}\text{H}_{54}\text{O}_2\text{Br}_2$ , 628.2491; found, 628.2472. Anal. Calcd for  $\text{C}_{32}\text{H}_{54}\text{O}_2\text{Br}_2$ : C, 60.95; H, 8.63; Br, 25.34. Found: C, 60.92; H, 8.62; Br, 25.48.

### 1,2-Bis(*n*-dodecyloxy)-4-ethynyl-benzene (S5)

A solution of **S4** (9.0 g, 14.3 mmol) in 150 mL of dry THF was cooled to  $-78^\circ\text{C}$  under Ar.  $^n\text{BuLi}$  (11.4 mL of 2.5 M solution in hexanes, 28.5 mmol) was added dropwise to the mixture and the resulting mixture was stirred at  $-78^\circ\text{C}$  for 1 h, allowed to warm up to room temperature and stirred at room temperature for additional 4 h. The reaction was quenched with a saturated aq.  $\text{NH}_4\text{Cl}$  and extracted with  $\text{Et}_2\text{O}$ . The organic layer was dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the product was further purified by column chromatography (silica gel, hexanes, then 50:1 hexanes/ $\text{CH}_2\text{Cl}_2$ ) to give a white solid (4.38 g, 65%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.04 (dd,  $J = 8.2$  Hz,  $J = 1.9$  Hz, 1H), 6.97 (d,  $J = 1.9$  Hz, 1H), 6.77 (d,  $J = 8.2$  Hz, 1H), 3.97 (t,  $J = 6.6$  Hz, 2H), 3.95 (t,  $J = 6.6$  Hz, 2H), 2.96 (s, 1H), 1.74–1.84 (m, 4H), 1.20–1.50 (m, 36H), 0.87 (t,  $J = 6.6$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  149.87, 148.45, 125.36, 116.91, 113.93, 112.91, 83.92, 75.39, 69.18, 69.05, 32.00, 29.78, 29.73, 29.70, 29.48, 29.45, 29.22, 26.08, 22.78, 14.22. HRMS-EI (m/z):  $[\text{M}]^+$  calcd for  $\text{C}_{32}\text{H}_{54}\text{O}_2$ , 470.4124; found, 470.4113. Anal. Calcd for  $\text{C}_{32}\text{H}_{54}\text{O}_2$ : C, 81.64; H, 11.56. Found: C, 81.36; H, 11.70.

### 4,4'-Di[3,4-bis(*n*-dodecyloxy)phenylethynyl]benzil (S6)

A Schlenk tube was charged with  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  (29.4 mg,  $7.7 \times 10^{-2}$  mmol),  $\text{CuI}$  (10 mg,  $5.1 \times 10^{-2}$  mmol), anhydrous 1,4-dioxane (30 mL),  $\text{P}^t\text{Bu}_3$  (0.31 g of 10 wt% solution in hexanes,  $1.5 \times 10^{-1}$  mmol),  $^i\text{Pr}_2\text{NH}$

(0.9 mL, 6.1 mmol), 4,4'-dibromobenzil (0.94 g, 2.6 mmol), and **S5** (3.0 g, 6.4 mmol) under Ar atmosphere. The reaction mixture was stirred at room temperature for 48 h. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through Celite. The solvent was removed under reduced pressure to give a yellowish brown solid. The product was purified by column chromatography (silica gel, 2:1 to 1:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) to give a yellow solid. The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes to give a yellow solid (2.39 g, 82%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.5 Hz, 4 H), 7.60 (d, *J* = 8.5 Hz, 4 H), 7.11 (dd, *J* = 8.5 Hz, 1.9 Hz, 2 H), 7.03 (d, *J* = 1.9 Hz, 2 H), 6.82 (d, *J* = 8.5 Hz, 2 H), 4.00 (t, *J* = 6.6 Hz, 4 H), 3.99 (t, *J* = 6.6 Hz, 4 H), 1.76–1.86 (m, 8 H), 1.20–1.51 (m, 72 H), 0.86 (t, *J* = 6.6 Hz, 12 H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 193.09, 150.22, 148.60, 131.67, 131.45, 130.54, 129.75, 125.33, 116.51, 114.16, 112.94, 94.91, 87.16, 69.26, 69.08, 32.00, 29.78, 29.75, 29.70, 29.46, 29.26, 29.22, 26.09, 22.80, 14.24. MS(EI) *m/z* 1148 (M<sup>+</sup>). Anal. Calcd for C<sub>78</sub>H<sub>114</sub>O<sub>6</sub>: C, 81.62; H, 10.01. Found: C, 81.54; H, 10.05.

## Nonlinear Optical Measurements

Solution 2PA spectra were measured using the open-aperture Z-scan technique [48,49]. A Ti:sapphire regenerative amplification system (CPA2010, CLARK-MXR), providing laser pulses at 775 nm with 140 fs duration (FWHM) at a 1 kHz repetition rate, was used to pump an optical parametric amplifier (OPA) systems (TOPAS, Light Conversion), which was used to tune the wavelength and attenuate the output energy to 10–300 nJ. For regions close to the 1PA resonance (close to the 2PA peak of the present compounds), where linear absorption is important, the open-aperture Z-scan cannot separate the pure 2PA from 1PA followed by excited-state absorption. Accordingly, we performed time-resolved analysis via pump and probe measurements at these wavelengths; this allows us to separate those effects due to the difference in the response time and to establish that the Z-scan signal does indeed represent 2PA; these measurements are described in more detail elsewhere [40].

## CONCLUSION

Heck and Sonogashira coupling can be used to synthesize the diketones 4,4'-di[3,4-bis(*n*-dodecyloxy)styryl]benzil and 4,4'-di[3,4-bis(*n*-dodecyloxy)phenylethynyl]benzil respectively from 4,4'-dibromobenzil and the appropriate styrene and phenylalkyne derivatives. The distyrylbenzil derivative can be converted to the corresponding extended

nickel bis(dithiolene) derivative through reaction with phosphorus pentasulfide followed by nickel(II) chloride, while under the same conditions the di(phenylethynyl)benzil gives an ill-defined polymeric material. The extended nickel bis(dithiolene) shows strong 2PA throughout the telecommunications region of the NIR which, coupled with the good photostability of this class of compounds [47] suggests possible applications in optical pulse suppression, all-optical beam stabilization, and dynamic-range compression in this wavelength range.

## REFERENCES

- [1] Moses, E. I. & Wu, F. Y. (1980). *Opt. Lett.*, **5**, 64.
- [2] Maloney, C., Byrne, H., Dennis, W. M., Blau, W., & Kelly, J. M. (1988). *Chem. Phys.*, **121**, 21.
- [3] Winter, C. S., Hill, C. A. S., & Underhill, A. E. (1991). *Appl. Phys. Lett.*, **58**, 107.
- [4] Winter, C. S., Oliver, S. N., Manning, R. J., Rush, J. D., Hill, C. A. S., & Underhill, A. E. (1992). *J. Mater. Chem.*, **2**, 443.
- [5] Kuebler, S. M. & Denning, R. G. (1996). *Chem. Phys. Lett.*, **250**, 120.
- [6] The 2PA cross-section of **2** was not explicitly reported in reference [4]. However, if one assumes that the measured values of  $\text{Im}(\chi^{(3)})$  are only due to 2PA, a cross-section of ca. 5000 GM at 1.06  $\mu\text{m}$  (a wavelength at which there is also significant 1PA) can be deduced for the material in the film.
- [7] Mizrahi, V., DeLong, K. W., Stegeman, G. I., Saifi, M. A., & Andrejco, M. J. (1989). *Opt. Lett.*, **14**, 1140.
- [8] Lin, T.-Z., Chung, S.-J., Kim, K.-S., Wang, X., He, G. S., Swiatkiewicz, J., Pudavar, H. E., & Prasad, P. N. (2003). *Adv. Polym. Sci.*, **161**, 157.
- [9] Albota, M., Beljonne, D., Brédas, J. L., Ehrlich, J. E., Fu, J.-Y., Heikal, A. A., Hess, S. E., Kogej, T., Levin, M. D., Marder, S. R., McCord-Maughon, D., Perry, J. W., Röckel, H., Rumi, M., Subramanian, G., Webb, W. W., Wu, X.-L., & Xu, C. (1998). *Science*, **281**, 1653.
- [10] Rumi, M., Ehrlich, J. E., Heikal, A. A., Perry, J. W., Barlow, S., Hu, Z., McCord-Maughon, D., Parker, T. C., Röckel, H., Thayumanavan, S., Marder, S. R., Beljonne, D., & Brédas, J. L. (2000). *J. Am. Chem. Soc.*, **122**, 9500.
- [11] Pond, S. J. K., Rumi, M., Levin, M. D., Parker, T. C., Beljonne, D., Day, M. W., Brédas, J. L., Marder, S. R., & Perry, J. W. (2002). *J. Phys. Chem. A*, **106**, 11470.
- [12] Yoo, J., Yang, S. K., Jeong, M.-Y., Ahn, H. C., Jeon, S.-J., & Cho, B. R. (2003). *Org. Lett.*, **5**, 645.
- [13] Strehmel, B., Sarker, A. M., & Detert, H. (2003). *Chem. Phys. Chem.*, **4**, 249.
- [14] Chung, S.-J., Rumi, M., Alain, V., Barlow, S., Perry, J. W., & Marder, S. R. (2005). *J. Am. Chem. Soc.*, **127**, 10844.
- [15] Chung, S.-J., Zheng, S., Odani, T., Beverina, L., Fu, J., Padilha, L. A., Biesso, A., Hales, J. M., Zhan, X., Schmidt, K., Ye, A., Zojer, E., Barlow, S., Hagan, D. J., Van Stryland, E. W., Yi, Y., Shuai, Z., Pagani, G. A., Brédas, J. L., Perry, J. W., & Marder, S. R. (2006). *J. Am. Chem. Soc.*, **128**, 14444.
- [16] Ventelon, L., Blanchard-Desce, M., Moreaux, L., & Mertz, J. (1999). *Chem. Commun.*, 2055.
- [17] Abboto, A., Beverina, L., Bozio, R., Facchetti, A., Ferrante, C., Pagani, G. A., Pedron, D., & Signorini, R. (2002). *Org. Lett.*, **4**, 1495.

- [18] Oliveira, S. L., Corrêa, D. S., Misoguti, L., Constantino, C. J. L., Aroca, R. F., Zilio, S. C., & Mendonça, C. R. (2005). *Adv. Mater.*, *17*, 1890.
- [19] Zheng, S., Leclercq, A., Fu, J., Beverina, L., Padilha, L. A., Zojer, E., Schmidt, K., Barlow, S., Luo, J., Jiang, S.-H., Jen, A. K.-Y., Yi, Y., Shuai, Z., Van Stryland, E. W., Hagan, D. J., Brédas, J. L., & Marder, S. R. (2007). *Chem. Mater.*, *19*, 432.
- [20] Belfield, K. D., Hagan, D. J., Van Stryland, E. W., Schaefer, K. J., & Negres, R. A. (1999). *Org. Lett.*, *1*, 1575.
- [21] Wang, X., Wang, D., Zhou, G. Y., Yu, W., Zhou, Y., Fang, Q., & Jiang, M. (2001). *J. Mater. Chem.*, *11*, 1600.
- [22] Antonov, L., Kamada, K., Ohta, K., & Kamounah, F. S. (2003). *Phys. Chem. Chem. Phys.*, *5*, 1193.
- [23] Beverina, L., Fu, J., Leclercq, A., Zojer, E., Pacher, P., Barlow, S., Van Stryland, E. W., Hagan, D. J., Brédas, J. L., & Marder, S. R. (2005). *J. Am. Chem. Soc.*, *127*, 7282.
- [24] Cho, B. R., Son, K. H., Lee, S. H., Song, Y.-S., Lee, Y.-K., Jeon, S.-J., Choi, J. H., Lee, H., & Cho, M. (2001). *J. Am. Chem. Soc.*, *123*, 10039.
- [25] Lee, W.-H., Lee, H., Kim, J.-A., Choi, J.-H., Cho, M., Jeon, S.-J., & Cho, B. R. (2001). *J. Am. Chem. Soc.*, *123*, 10658.
- [26] Beljonne, D., Wenseleers, W., Zojer, E., Shuai, Z., Vogel, H., Pond, S. J. K., Perry, J. W., Marder, S. R., & Brédas, J. L. (2002). *Adv. Funct. Mater.*, *12*, 631.
- [27] Cassoux, P. & Valade, L. (1996). Molecular inorganic superconductors. In: *Inorganic Materials*, 2nd Edition, Bruce, D. W. & O'Hare, D. (Eds.), Wiley: Chichester.
- [28] Pearson, C., Gibson, J. E., Moore, A. J., Bryce, M. R., & Petty, M. C. (1993). *Electronics Lett.*, *29*, 1377.
- [29] Tagushi, T., Wada, H., Kambayashi, T., Noda, B., Goto, M., Mori, T., Ishikawa, K., & Takezoe, H. (2006). *Chem. Phys. Lett.*, *421*, 395.
- [30] Anthopoulos, T. D., Setayesh, S., Smits, E., Colle, M., Cantatore, E., de Boer, B., Blom, P. W. M., & de Leeuw, D. M. (2006). *Adv. Mater.*, *18*, 1900.
- [31] Cho, J.-Y., Domercq, B., Yu, J., Zhang, X., Jones, S. C., An, Z., Bishop, M., Barlow, S., Marder, S. R., & Kippelen, B. *J. Mater. Chem.*, in press.
- [32] Kurotobi, K., Kim, K. S., Noh, S. B., Kim, D., & Osuka, A. (2006). *Angew. Chem. Int. Ed.*, *45*, 3944.
- [33] Drobizhev, M., Stepanenko, Y., Rebane, A., Wilson, C. J., Screen, T. E. O., & Anderson, H. L. (2006). *J. Am. Chem. Soc.*, *128*, 12432.
- [34] Spangler, C. W. (1999). *J. Mater. Chem.*, *9*, 2013.
- [35] Tay, S., Thomas, J., Eralp, M., Li, G., Kippelen, B., Marder, S. R., Meredith, G., Schülzgen, A., & Peyghambarian, N. (2004). *Appl. Phys. Lett.*, *85*, 4561.
- [36] Tay, S., Thomas, J., Eralp, M., Li, G., Norwood, R. A., Schülzgen, A., Yamamoto, M., Barlow, S., Walker, G. A., Marder, S. R., & Peyghambarian, N. (2005). *Appl. Phys. Lett.*, *87*, 171105.
- [37] Schrauzer, G. & Mayweg, V. P. (1965). *J. Am. Chem. Soc.*, *87*, 1483.
- [38] Ohta, K., Hasebe, H., Ema, H., Fujimoto, T., & Yamamoto, I. (1989). *J. Chem. Soc., Chem. Commun.*, 1610.
- [39] Ohta, K., Inagaki-Oka, Y., Hasebe, H., & Yamamoto, I. (2000). *Polyhedron*, *19*, 267.
- [40] Cho, J.-Y., Barlow, S., Marder, S. R., Fu, J., Padilha, L. A., Van Stryland, E. W., Hagan, D. J., & Bishop, M. (2007). *Opt. Lett.*, *32*, 671.
- [41] Kosteyn, F., Zerban, G., & Meier, H. (1992). *Chem. Ber.*, *125*, 893.
- [42] Gehringer, L., Guillon, D., & Donnio, B. (2003). *Macromolecules*, *36*, 5593.
- [43] Gehringer, L., Bourgogne, C., Guillon, D., & Donnio, B. (2004). *J. Am. Chem. Soc.*, *126*, 3856.
- [44] Le Bigot, Y., Delmas, M., & Gaset, A. (1982). *12*, 107.

- [45] Pelter, A., Ward, R. S., & Little, G. M. (1990). *J. Chem. Soc. Perkin. Trans.*, 1, 2775.
- [46] Yin, L. & Liebscher, J. (2007). *Chem. Rev.*, 107, 133.
- [47] Mueller-Westerhoff, U. T., Vance, B., & Yoon, D. I. (1991). *Tetrahedron*, 47, 909.
- [48] Sheik-bahae, M., Said, A. A., & Van Stryland, E. W. (1989). *Opt. Lett.*, 14, 955.
- [49] Sheik-bahae, M., Said, A. A., Wei, T.-H., Hagan, D. J., & Van Stryland, E. W. (1990). *IEEE J. Quantum. Electron.*, 26, 760.
- [50] For another example where extension of a  $\pi$  system affects transition dipole moment terms more strongly than energy terms, and consequently where the former terms dominate the evolution of NLO properties, see: Hu, Z.-Y., Fort, A., Barzoukas, M., Jen, A. K.-Y., Barlow, S., & Marder, S. R., (2004) *J. Phys. Chem. B*, 108, 8626.