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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 = 10⁻⁵⁰ cm⁴ s photon⁻¹ molecule⁻¹) 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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2 were reported to have large values of the real parts of the third-order susceptibility, Re(χ³), at 1.06 μm, 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(dithiolenes); 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 μm [4,6], since Im(χ³), to which 2PA is often a major contributor, is detrimental for all-optical switching, with Re(χ³)/Im(χ³) 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 Re(χ³). π-Conjugated chromophores with various structural motifs incorporating π-donors (D) and π-acceptors (A) have been shown to exhibit high peak 2PA cross-sections, δ_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 [X]ₙ[M(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

![FIGURE 1 Structures of some nickel bis(dithiolene)s discussed in the text.](image)
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 \( \mu \)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 = \( 10^{-50} \) cm\(^4\) s photon\(^{-1}\) 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 Gerhringer’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′-dibromo-benzil with the terminal alkene or alkyne under Heck or Sonogashira conditions, respectively [46].
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 \textit{in situ} reducing agents; we adopted this approach, initially forming the dithiones \textit{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 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; $^1$H NMR spectroscopy suggested that there were

\textbf{FIGURE 2} Synthesis of new diketones with extended conjugation and alkoxy donors.
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 \(^4\)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),

![Graph](image-url)
corresponding to photon energies of ca. 1.0 eV and to photon wavelengths of ca. 1.2 μm. 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 μm 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

\[
\delta \propto E_{ge}^2 \frac{\mu_{ge}^2 \mu_{ee'}^2}{(E_{ge} - (E_{ge}/2))^2}
\]

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

\[
\mu_{ge} = 0.09584 \sqrt{\frac{\int \varepsilon(\nu)d\nu}{\nu_{\text{max}}}}
\]

where \( \nu_{\text{max}} \) and \( \varepsilon(\nu) \) are in cm\(^{-1}\) and M\(^{-1}\) cm\(^{-1}\) 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 \( \delta_{\text{max}} \) by a factor of ca. 2 between 4 and 5, whereas the experimental values of \( \delta_{\text{max}} \) 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 \( \delta_{\text{max}} \)
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$_2$CO$_3$ (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$_2$ atmosphere. Water was added and the mixture was extracted with CH$_2$Cl$_2$. The organic layer was washed with water and saturated aq. NaCl several times and dried over MgSO$_4$. 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. $^1$H NMR (200 MHz, CDCl$_3$) δ 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). $^{13}$C{$_1$H} NMR (200 MHz, CDCl$_3$) δ 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$^{-1}$): 2916, 2847, 1686, 1672, 1584, 1506, 1277, 1236, 1133, 807, 800. HRMS (FAB) calcd for C$_{31}$H$_{55}$O$_3$ (MH$^+$), 475.4151; found, 475.4156. Anal. Calcd for C$_{31}$H$_{54}$O$_3$: C, 78.43; H, 11.46. Found: C, 78.46; H, 11.72.

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

A mixture of Ph$_3$PMeBr (8.79 g, 24.6 mmol), K$_2$CO$_3$ (3.4 g, 24.6 mmol), S1 (10.0 g, 21.1 mmol), 1,4-dioxane (25 mL), and H$_2$O (0.3 mL) was refluxed for 24 h, allowed to cool to room temperature, and extracted with CH$_2$Cl$_2$. The organic extracts were washed with H$_2$O, dried over MgSO$_4$, evaporated under reduced pressure, and purified by column chromatography (silica gel, 2:1 hexanes/CH$_2$Cl$_2$) to give S2 as a white solid (6.53 g, 66%). $^1$H NMR (300 MHz, CDCl$_3$) δ 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). $^{13}$C{$_1$H} NMR (75 MHz, CDCl$_3$) δ 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$_{32}$H$_{56}$O$_2$, 472.4280; found, 472.4267. Anal. Calcd C$_{32}$H$_{56}$O$_2$: 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), K2CO3 (3.38 g, 24.5 mmol), Bu4NBr (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 CH2Cl2. The organic extracts were washed with H2O, dried over MgSO4, evaporated under reduced pressure, and purified by column chromatography (silica gel, 1:2 to 3:2 CH2Cl2/hexanes) and recrystallization from CH2Cl2/hexanes to give S2 as a bright yellow solid (4.27 g, 76%). 1H NMR (300 MHz, CDCl3) δ 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, 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). 13C{1H} NMR (75 MHz, CDCl3) δ 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 C78H118O6: C, 81.34; H, 10.33. Found: C, 81.25; H, 10.35.

Compound 5

S3 (1.0 g, 0.87 mmol), P2S5 (0.58 g, 1.3 mmol), and p-dioxane (20 mL) were refluxed for 5 h under N2, allowed to cool to 60°C, and filtered under N2. NiCl2 · 6H2O (0.103 g, 0.43 mmol) in H2O (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 CH2Cl2. The organic extracts were washed with H2O, dried over anhydrous MgSO4 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/CH2Cl2) to give a dark green solid, 5 (0.314 g, 30%). 1H NMR (300 MHz, CDCl3) δ 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). 13C{1H} NMR (75 MHz, CDCl3) δ 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 CBr4 (6.99 g, 21.1 mmol) in dry CH2Cl2 at 0°C was added PPh3 (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 CH₂Cl₂, washed with H₂O, and dried over anhydrous MgSO₄. 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/CH₂Cl₂) to give a yellowish white solid (11.37 g, 86%). ¹H NMR (300 MHz, CDCl₃)  δ 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). ¹³C{¹H} NMR (75 MHz, CDCl₃)  δ 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 C₃₂H₅₄O₂Br₂, 628.2491; found, 628.2472. Anal. Calcd for C₃₂H₅₄O₂Br₂: 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°C under Ar. ²⁷BuLi (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°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. NH₄Cl and extracted with Et₂O. The organic layer was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the product was further purified by column chromatography (silica gel, hexanes, then 50:1 hexanes/CH₂Cl₂) to give a white solid (4.38 g, 65%). ¹H NMR (300 MHz, CDCl₃)  δ 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). ¹³C{¹H} NMR (75 MHz, CDCl₃)  δ 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): [M]⁺ calcd for C₃₂H₅₄O₂, 470.4124; found, 470.4113. Anal. Calcd for C₃₂H₅₄O₂Br₂: C, 60.95; H, 8.63; Br, 25.34. Found: C, 60.92; H, 8.62; Br, 25.48.

4,4’-Di[3,4-bis(n-dodecyloxy)phenylethynyl]benzil (S6)

A Schlenk tube was charged with Pd(PhCN)₂Cl₂ (29.4 mg, 7.7 × 10⁻² mmol), CuI (10 mg, 5.1 × 10⁻² mmol), anhydrous 1,4-dioxane (30 mL), P⁴Bu₃ (0.31 g of 10 wt% solution in hexanes, 1.5 × 10⁻¹ mmol), ⁴Pr₂NH
(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 CH₂Cl₂ 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/CH₂Cl₂) to give a yellow solid. The solid was recrystallized from CH₂Cl₂/hexamnes to give a yellow solid (2.39 g, 82%). ¹H NMR (300 MHz, CDCl₃) 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). ¹³C{¹H} NMR (75 MHz, CDCl₃) 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⁺). Anal. Calcd for C₇₈H₁₁₄O₆: C, 81.62; H, 10.01. Found: C, 81.54; H, 10.05.

Nonlinear Optical Measurements

Solution 2 PA 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 1 PA resonance (close to the 2 PA peak of the present compounds), where linear absorption is important, the open-aperture Z-scan cannot separate the pure 2 PA from 1 PA 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 2 PA; 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(phenylethylnyl)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 supression, all-optical beam stabilization, and dynamic-range compression in this wavelength range.

REFERENCES

[6] The 2PA cross-section of 2 was not explicitly reported in reference [4]. However, if one assumes that the measured values of Im(\(\gamma_3\)) are only due to 2PA, a cross-section of ca. 5000 GM at 1.06\(\mu\)m (a wavelength at which there is also significant 1PA) can be deduced for the material in the film.


Two-Photon Absorbing Nickel Bis(dithiolene)