SUPPORTING INFORMATION

Strong, Low-Energy Two-Photon Absorption in Extended Amine-Terminated Cyano-Substituted Phenylenevinylene Oligomers

Sung-Jae Chung, Mariacristina Rumi, Valérie Alain, Stephen Barlow, Joseph W. Perry,* and Seth R. Marder*

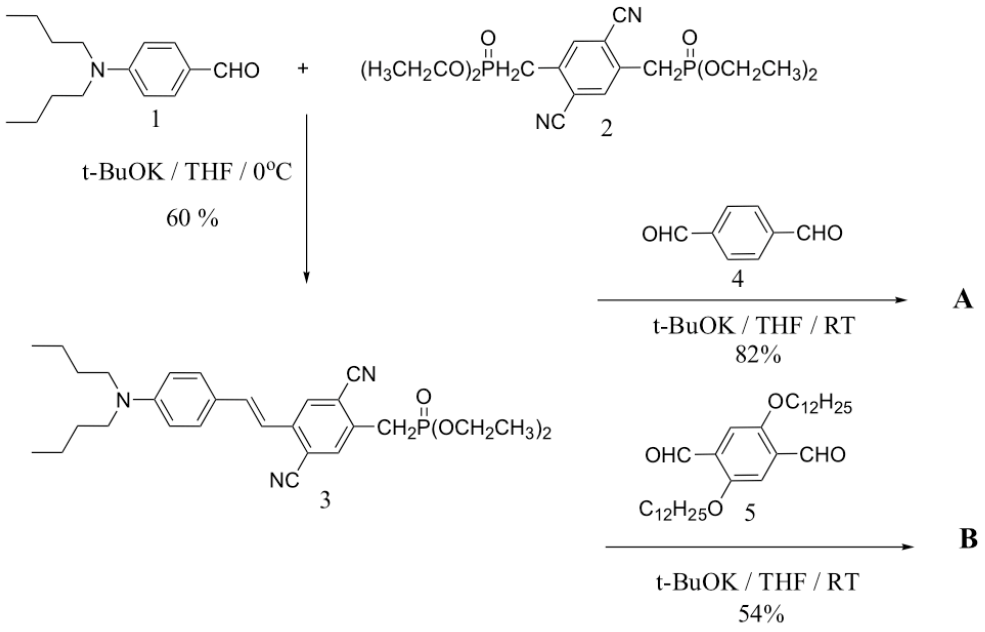
Contribution from the School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332; and Department of Chemistry, University of Arizona, Tucson, AZ 85721

Synthesis and Characterization. The synthesis of compounds **A**-**C** was accomplished using Horner-Emmons reactions between phosphonate ylids and benzaldehyde derivatives, to form exclusively *trans* oligo(phenylenevinylenes). In the final steps, compounds **A** and **B** were synthesized by the condensation of the phosphonate compound **3** with dialdehyde derivatives in 82 % and 54 % yields, respectively (Scheme 1). For the synthesis of compound **C**, the intermediate **8** was prepared by reacting 2,5-dimethoxy terephthaldehyde and phosphonate **7** (Scheme 2). A Horner-Emmons coupling of **8** with the diphosphonate **2** in THF gave compound **C** in 61 % yield.

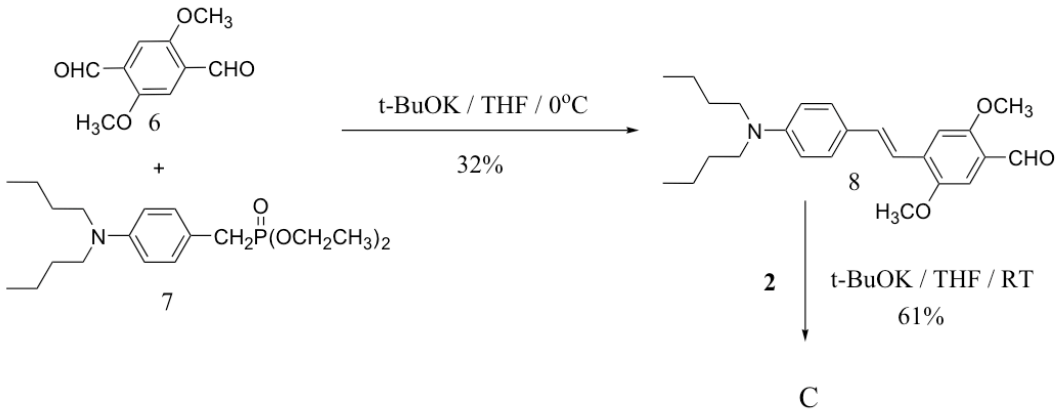
All solvents and reagents were purchased from Aldrich as reagent grade and used as received. Gas chromatography detected by mass spectrometry (GC-MS) was performed on an HP 6890 gas chromatograph equipped with a HP 5973 mass selective detector. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA, or by Desert Analytics, Tucson, AZ. NMR spectra were recorded on a Varian Mercury Vx 300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) or on a Bruker DRX 500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C). The reported yields are isolated

yields. High-resolution mass spectroscopy was performed at the Department of Chemistry, University of Arizona, Tucson, AZ.

Scheme 1:



Scheme 2:



2-[(4-(*N*,*N*-Dibutylamino)phenyl)vinyl]-5-(diethoxyphosporyl)methylterephthalo-nitrile, 3: To a solution of 4-(*N,N*-dibutylamino)phenylcarboxaldehyde (1.0 g, 4.3 mmol) and tetraethyl-(2,5-dicyano-α,α'-*p*-xylylenediphosphonate)[1] (2.0 g, 4.7 mmol) in THF (100 mL) at 0 ^{o}C was added to suspension of potassium *tert*-butoxide (6 mL of 1.6 M in THF). The suspension was stirred at 0 ^{o}C for 30 min and then water (1 mL) was added to stop the reaction. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel, eluting with methylene chloride to obtain 1.3 g (60%) of product. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.99 (s, 1H), 7.70 (d, J = 3.0 Hz, 1H), 7.44 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 16.0 Hz, 1H), 7.07 (d, J = 16.0 Hz, 1H), 6.63 (d, J = 8.7 Hz, 2H), 4.14 (m, 4H), 3.39 (d, J = 27.0 Hz, 2H), 3.32 (t, J = 7.6 Hz, 4H), 1.59 (m, 4H), 1.32 (m, 10H), 0.97 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.46, 141.28 (d, J_{CP} = 6.0 Hz), 136.18 (d, J_{CP} = 6.0 Hz), 135.19 (d, J_{CP} = 9.1 Hz), 132.29 (d, J_{CP} = 5.3 Hz), 129.43, 128.93 (d, J_{CP} = 2.3 Hz), 122.42, 117.61 (d, J_{CP} = 5.3 Hz), 116.88 (d, J_{CP} = 8.3 Hz), 116.81, 115.90, 113.63 (d, J_{CP} = 8.7 Hz), 111.73, 62.98 (d, J_{CP} = 5.3 Hz), 51.33, 32.27, 30.36 (d, J_{CP} = 139 Hz), 22.96, 16.58 (d, J_{CP} = 7.5 Hz), 14.46. HRMS(FAB) calcd for $C_{29}H_{39}N_3O_3P$ ($[M+H]^+$): 508.2729, found: 508.2721. Anal. Calcd for $C_{29}H_{38}N_3O_3P$: C, 68.62; H, 7.55; N, 8.28, found: C, 68.64, H, 7.45, N, 8.28.

1,4-Bis(2-{4-[2-(4-(*N*,*N*-dibutylamino)phenyl)vinyl]-2,5-dicyanophenyl}vinyl) benzene, A: To a solution of terephthalcarboxaldehyde (90.0 mg, 0.67 mmol) and compound **3** (700 mg, 1.38 mmol) in THF (30 mL) was added potassium *tert*-butoxide (1.0 g, 8.0 mmol); after 3 h, water (1 mL) was added to stop the reaction. The solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel, eluting with methylene chloride; the resulting solid was purified further by recrystallization from toluene. The yield of product was 0.46 g (82%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93 (s, 2H), 7.92 (s, 2H), 7.54 (s, 4H), 7.38 (d, J = 8.5

Hz, 4H), 7.30 (d, J = 16.0, 2H), 7.19 (m, 4H), 7.05 (d, J = 16.0 Hz, 2H), 6.57 (d, J = 9.0 Hz, 4H), 3.25 (t, J = 7.8 Hz, 8H), 1.52 (quint, J = 7.0 Hz, 8H), 1.32 (sext, J = 7.5 Hz, 8H), 0.91 (t, J = 7.3 Hz, 12H). ^{13}C NMR ($CDCl_2CDCl_2$, 75 MHz) δ 149.77, 140.93, 137.27, 137.02, 136.16, 133.67, 130.44, 129.87, 129.56, 128.42, 123.26, 122.64, 117.69, 117.63, 116.37, 115.46, 114.38, 112.09, 51.45, 30.17, 21.14, 14.93. HRMS (FAB) calcd for $C_{58}H_{61}N_6$ ([M+H]$^+$): 841.4958, found: 841.4960. Anal. Calcd for $C_{58}H_{60}N_6$: C, 82.82, H, 7.19, N, 9.98, found: C, 82.77, H, 7.57, N, 9.63.

1,4-Bis(2-{4-[2-(4-(*N*,*N*-dibutylamino)phenyl)vinyl]-2,5-dicyanophenyl}vinyl)-2,5-didodecyloxybenzene, B: To a solution of 2,5-didodecyloxy terephthaldehyde[2] (250 mg, 0.49 mmol) and compound **3** (500 mg, 0.99 mmol) in THF (20 mL) was added potassium *tert*-butoxide (500 mg, 4 mmol); after 2 h, water (1 mL) was added to stop the reaction. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel, eluting with methylene chloride. The resulting solid was purified further by recrystallization from toluene. The yield of product was 320 mg (54%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.01 (s, 2H), 8.00 (s, 2H), 7.60 (d, J = 16.0 Hz, 2H), 7.49 (d, J = 16.0 Hz, 2H), 7.48 (d, J = 9.0 Hz, 4H), 7.26 (d, J = 16.0 Hz, 2H), 7.14 (d, J = 16.0 Hz, 2H), 7.13 (s, 2H), 6.67 (d, J = 8.5 Hz, 4H), 4.13 (t, J = 6.5 Hz, 4H), 3.35 (t, J = 7.7 Hz, 8H), 1.98 (t, J = 7.5 Hz, 4H), 1.65 (quint, J = 7.3 Hz, 8H), 1.59 (quint, J = 7.8 Hz, 4H), 1.45 (m, 8H), 1.38 (m, 32H), 1.02 (t, J = 7.5 Hz, 12H), 0.91 (t, J = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_2CDCl_2$, 75 MHz) δ 151.56, 149.11, 139.92, 137.71, 134.57, 131.84, 129.79, 129.21,129.03, 128.97, 126.40, 123.64, 122.13, 117.26, 117.14, 115.30, 114.82, 113.75, 111.49, 69.47, 50.85, 32.12, 29.89, 29.58, 26.49, 22.95, 20.54, 14.50, 14.33 (remaining alkyl ^{13}C peaks presumably obscured by overlap). HRMS (FAB) calcd for $C_{82}H_{109}N_6O_2$ ([M+H])$^+$: 1209.8612, found: 1209.8634. Anal. Calcd for $C_{82}H_{108}N_6O_2$: C, 81.41, H, 8.99, N, 6.94, found: C, 81.07, H, 9.02, N, 6.90.

4-[2-(4-(*N,N*-Dibutylamino)phenyl)vinyl]-2,5-dimethoxybenzaldehyde, 8: To a solution of 2,5-dimethoxy terephthaldehyde (1.37 g, 7.0 mmol) and *N, N*-dibutylamino-4-(diethoxy phosphoryl)methylbenzene[3] (2.5 g, 7.0 mmol) in THF (50 mL) at 0 ^{o}C was added potassium *tert*-butoxide (1.0 g, 8.0 mmol). The suspension was stirred at 0 ^{o}C for 2 h and then water (1 mL) was added to stop the reaction. The mixture was poured into water and extracted with ethyl acetate. The organic solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (10:1) to obtain 0.88 g (32%) of product. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.38 (s, 1H), 7.42 (d, J = 9.0 Hz, 2H), 7.29 (s, 1H), 7.24 (d, J = 16.5 Hz, 1H), 7.15 (s, 1H), 7.13 (d, J = 16.5 Hz, 1H), 6.61 (d, J = 9.0 Hz, 2H), 3.94 (s, 3H), 3.86 (s, 3H), 3.28 (t, J = 7.7 Hz, 4H), 1.57 (quint, J = 7.8 Hz, 4H), 1.36 (sext, J = 7.5 Hz, 4H), 0.95 (t, J = 7.2 Hz, 6H). ^{13}C ($CDCl_3$, 75 MHz) δ 188.66, 156.66, 150.60, 148.17, 135.48, 132.74, 128.34, 124.01, 122.78, 116.83, 111.38, 108.87, 108.15, 56.10, 56.04, 50.77, 29.51, 20.40, 14.10. GC/MS *m/z* 395 (M^+). Anal. Calcd for $C_{25}H_{33}NO_3$: C, 75.91; H, 8.41, N, 3.54, found: C, 76.06, H, 8.48, N, 3.62.

2,5-Bis(2-{4-[2-(4-(*N,N*-dibutylamino)phenyl)vinyl]-2,5-dimethoxyphenyl}vinyl)-terephthalonitrile, C: To a solution of compound **8** (1.0 g, 2.5 mmol) and tetraethyl-(2,5-dicyano-α,α'-*p*-xylylenediphosphonate) (530 mg, 1.25 mmol) in THF (30 mL) was added potassium *tert*-butoxide; the reaction was stirred for 2 hr and then water (1 mL) was added to stop the reaction. The solvent was removed and the crude product was purified by column chromatography on silica gel, eluting with methylene chloride. The resulting solid was purified further by recrystallization from a mixture of toluene, methylene chloride and hexane (10:2:3). The yield of product was 0.7 g (61%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.99 (s, 2H), 7.58 (d, J = 16.0 Hz, 2H), 7.35 (d, J = 9.0 Hz, 4H), 7.32 (d, J = 16.5 Hz, 2H), 7.18 (d, J = 16.5 Hz, 2H), 7.06 (s, 2H), 7.04 (s, 2H), 7.00 (d, J = 16.5 Hz, 2H), 6.55 (d, J = 9.0 Hz, 4H), 3.90 (s, 6H), 3.85 (s, 6H), 3.22 (q, J = 7.6

Hz, 8H), 1.53 (quint, J = 7.8 Hz, 8H), 1.30 (sext, J = 7.5 Hz, 8H), 0.90 (t, J = 7.3 Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.24, 150.84, 147.82, 138.95, 129.95, 129.29, 127.96, 124.57, 123.02, 120.87, 117.41, 116.91, 114.57, 111.53, 109.64, 109.51, 108.09, 107.96, 56.48, 56.18, 50.81, 29.57, 20.44, 14.11. HRMS (FAB) calcd for $C_{60}H_{71}N_4O_4$ ($[M+H]^+$): 911.5475, found: 911.5471. Anal. Calcd for $C_{60}H_{70}N_4O_4$, C, 79.10, H, 7.74, N, 6.16, found: C, 78.78, H, 7.59, N, 6.09.

Linear Spectroscopy. All spectroscopic measurements were performed in toluene (spectrophotometric grade, from Aldrich). UV-Visible absorption spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer. Extinction coefficients, ε_{max}, were measured on multiple solutions obtained by dilution of two or three stock solutions. The measurements were performed using cuvettes with pathlengths between 0.1 and 1 cm. The solutions analyzed had concentrations between about 1×10^{-6} and 2×10^{-4} M (except for **A**, where the highest concentration was 2.5×10^{-5} due to limited solubility). The uncertainty on the values reported is below 2%. Fluorescence emission spectra were collected using a Spex Fluorolog II fluorimeter (F112AI). Quantum yields, η, were determined on optically dilute solutions[4] using rhodamine 101 in ethanol (η = 1.0)[5,6] and rhodamine 6G in ethanol (η = 0.94)[6-8] as references. The values of η reported in Table 1 of the paper are the average between the two determinations and have an uncertainty of about 5%. The linear absorption and fluorescence emission spectra of compounds **A-C** are displayed in Figures S.1 and S.2.

Two-photon Absorption Cross-Section Measurements. A relative two-photon–induced fluorescence method[9,10] was employed for the measurement of two-photon absorption cross sections, δ, using femtosecond and nanosecond pulsed lasers as excitation sources. Using a reference (r) chromophore for the two-photon cross-section measurement, the value of δ for a sample (s) is given by:

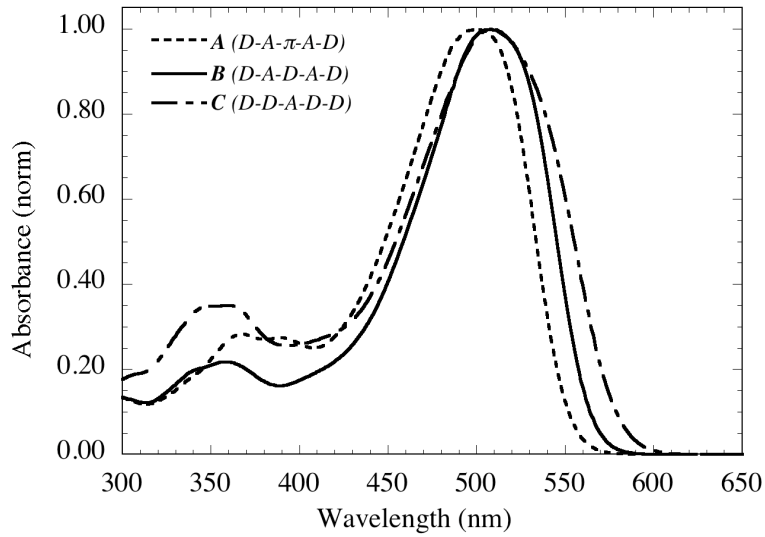


Figure S.1: Normalized absorption spectra of compounds **A**, **B**, and **C** in toluene.

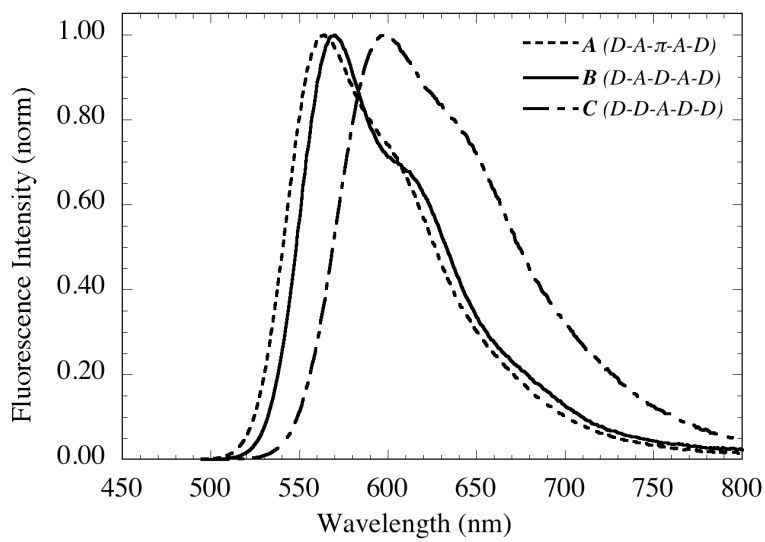


Figure S.2: Normalized fluorescence emission spectra of compounds **A**, **B**, and **C** in toluene.

$$\delta_s = \frac{S_s \eta_r \phi_r N_r}{S_r \eta_s \phi_s N_s} \delta_r$$

where S is the detected two-photon induced fluorescence signal and N is the concentration of the chromophore. ϕ is the collection efficiency of the experimental

setup and accounts for the wavelength dependence of the detectors and optics as well as the difference in refractive indices between the solvents in which the reference and sample compounds are dissolved.[10] The measurements were conducted in a regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for two-photon–induced emission. The experimental error on the reported cross section is 15-20%.

For the femtosecond-pulse experiment, the two-photon cross sections were measured using a Ti:Sapphire laser (Spectra-Physics, Tsunami) as the excitation source (pulse duration: 90 fs; repetition rate: 82 MHz; wavelength range: 720-1000 nm).[1] The concentration of the solutions was in the range 6 - 9 × 10^{-6} M for compounds **A** and 2 - 3 × 10^{-5} M for the reference chromophores. The collection of the two-photon–induced fluorescence signal was performed at the same detection wavelength for reference and sample compounds (either 560 or 580 nm). The output signal was averaged for 60 seconds for each excitation wavelength and sample. The nanosecond-pulse experiment[10] used the output of a tunable optical parametric oscillator (Quanta-Ray, MOPO 730) pumped by the third harmonic of a Q-switched Nd:YAG laser (Quanta Ray, PRO 250). The pulse duration is 5 ns and the repetition rate 10 Hz. The concentrations were in the range 2 - 7 × 10^{-5} M. The data were averaged over 600 pulses for each excitation wavelength and sample. The reference standards used were fluorescein (in water, pH 11), rhodamine B (in methanol) and coumarin 307 (in methanol).[9] The agreement between the results obtained using fs and ns excitation sources is quite satisfactory, as can be judged for the case of compound **A** in Figure S.3.

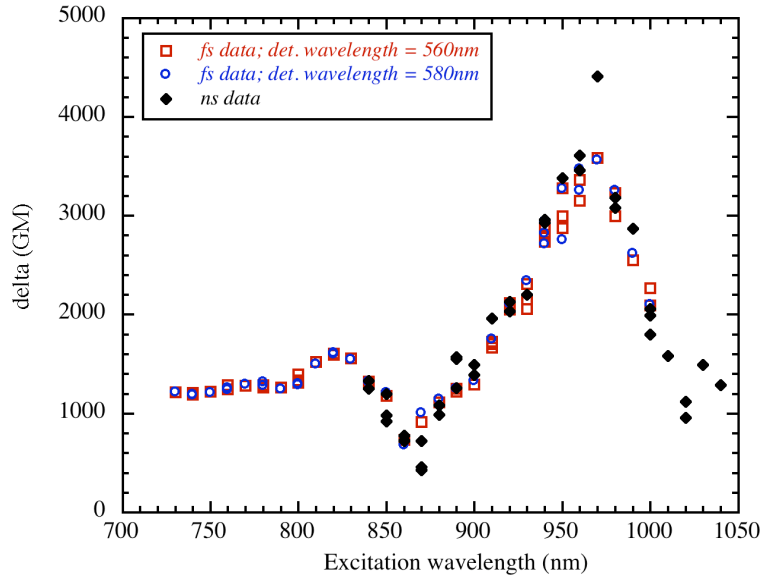


Figure S.3: Two-photon induced excitation spectra of compound **A** in toluene. Data obtained using ns and fs pulsed excitation sources are reported (reference material = fluorescein).

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Ref. 7:

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