Supplementary Information for:

Strong Two-Photon Absorption at Telecommunications Wavelengths in a Dipolar Chromophore with a Pyrrole Auxiliary Donor and Thiazole Auxiliary Acceptor

Luca Beverina, Jie Fu, Amalia Leclercq, Egbert Zojer, Peter Pacher, Stephen Barlow, Eric W. Van Stryland, David J. Hagan, Jean-Luc Brédas, and Seth R. Marder

1. Full Citations for "*et al.*" References from Main Paper

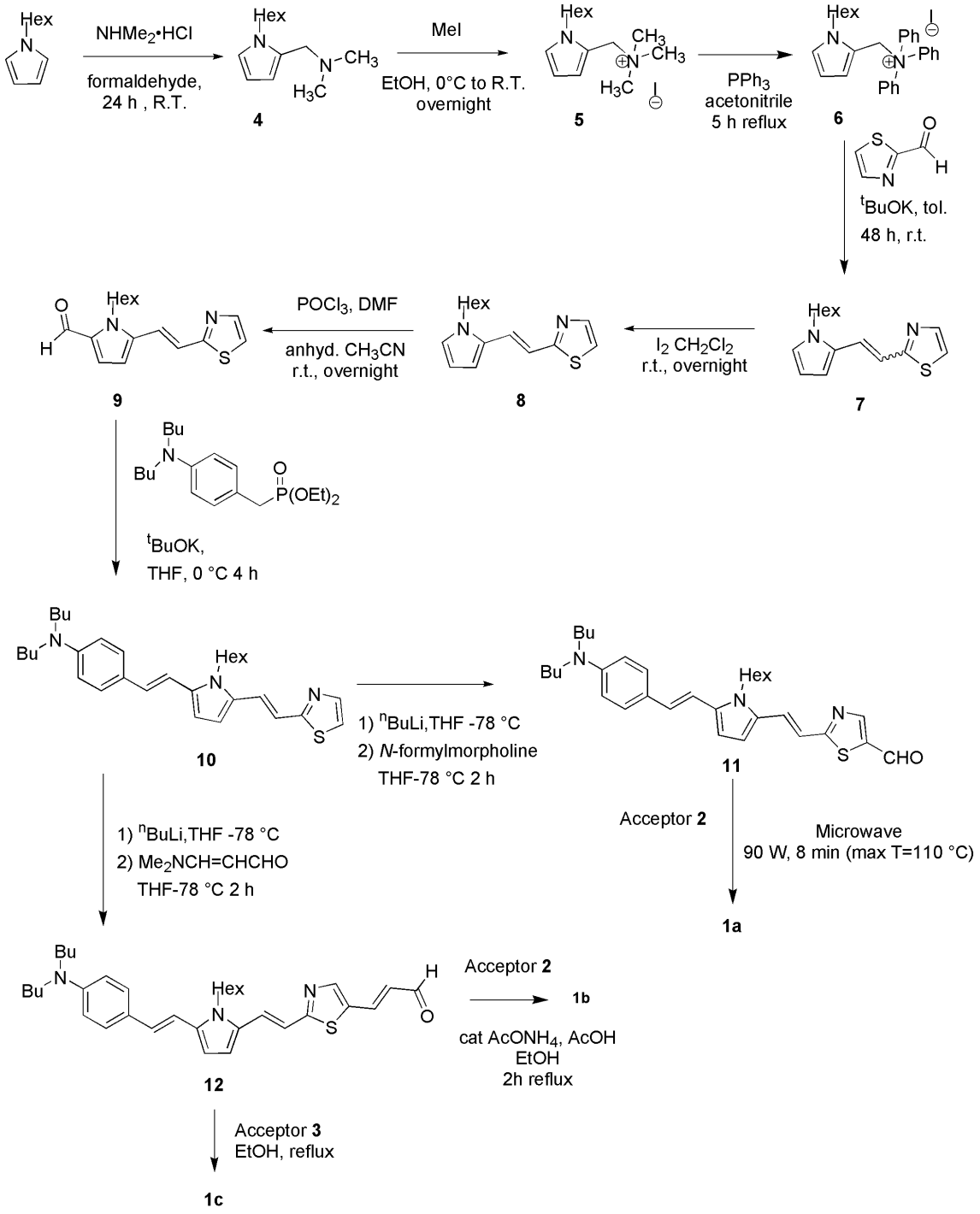
Reference 4b: Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I.-Y. S.; McCord-Maughon, D.; Qin, J.; Röckel, H.; Rumi, M.; Wu, X.-L.; Marder, S. R.; Perry, J. W., *Nature* **1999,** *398*, 51-54.

Reference 6a: 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., *Science* **1998**, *291*, 1635-1656.

2. Synthetic Details and Characterizing Data

Compounds **1a-c** were synthesized as shown in Scheme 1.

Scheme S1.



(1-Hexyl-1H-pyrrol-2-ylmethyl)-dimethyl-amine (4).[1] A solution of dimethylamine hydrochloride (13.600 g, 166.74 mmol) in 37% aqueous formaldehyde (15.1 ml, 170.00 mmol) was added to *N*-hexylpyrrole (25.200 g, 166.74) and the resulting biphasic mixture was stirred at room temperature overnight. The now clear and homogeneous solution was poured into 100 ml of 10% NaOH and extracted with Et_2O (3 × 50 mL). The organic phase was washed with water (100 mL), dried over $MgSO_4$ and evaporated, yielding 30.90 g of a colorless oil that was used directly in the next step without further purification. ^{1}H NMR ($CDCl_3$) δ 6.64 (d, *J* = 2.55 Hz, 1H), 6.05 (d, *J* = 3.35 Hz, 1H), 5.97 (dd, *J* = 3.33, 1.49 Hz, 1H), 3.93 (t, *J* = 7.44 Hz, 2H), 3.33 (s, 2H), 2.19 (s, 6H), 1.74 (quint, *J* = 7.47 Hz, 2H), 1.31 (m broad, 6H), 0.90 (t broad, 3H).

(1-Hexyl-1H-pyrrol-2-ylmethyl)-trimethyl-ammonium iodide (5). A solution of MeI (20.720 g, 146.00 mmol) in absolute ethanol (50 ml) was added dropwise and at 0 °C to a solution of **4** in 100 mL of the same solvent. Reaction mixture was stirred overnight at room temperature observing precipitation of a white solid. The precipitate was filtered and washed with cold ethanol (20 mL) affording the title compound as a white powder (33.090 g, 75.7% yield). The compound was used directly for the next step.

(1-Hexyl-1H-pyrrol-2-ylmethyl)-triphenyl-phosphonium iodide (6). Iodide, **5** (27.000 g, 77.08 mmol) and triphenylphosphine (23.610 g, 90.00 mmol) were suspended into 100 mL of acetonitrile. Mixture was refluxed for 5 h then cooled in an ice bath. The precipitate was filtered under reduce pressure and washed with hexane (100 mL) affording directly the pure title compound as a white powder (37.740 g, 88.4). ^{1}H NMR (DMSO-d_6) δ 7.89 (td, *J* = 7.8, 1.5 Hz, 3H), 7.86-7.68 (m, 6H), 7.67-7.57 (m, 6H), 6.76 (m, 1H), 5.88 (t, *J* = 3.9 Hz, 1H), 5.47 (m broad, 1H), 5.16 (d, *J* = 13.8 Hz, 2H), 3.301 (t, *J* = 6.9 Hz, 2H), 1.305 (quint, *J* = 7.8, 2H), 1.20-0.97 (m broad, 6H), 0.77 (t, *J* = 7.2 Hz, 3H). Anal. Calcd for $C_{29}H_{33}NPI$: C, 62.93; H, 6.01; N, 2.53; Found: C, 62.73; H, 6.11; N, 2.67.

2-[2-(1-Hexyl-1H-pyrrol-2-yl)-vinyl]-thiazole, mixture of *E*/*Z* (7). The phosphonium iodide **6** (27.70 g, 50.00 mmol) was suspended under nitrogen in 500 mL of anhydrous toluene. ^{t}BuOK (6.170 g, 55.00 mmol) was added directly as a solid and the resulting purple suspension was stirred at room temperature for 2.5 h. A solution of thiazole-2-carboxaldehyde (7.500 g, 66.3 mmol) in toluene (20 mL) was added dropwise and the

resulting brown suspension was stirred at room temperature over a week end. Mixture was poured into 500 mL of water, phases were separated and the aqueous layer was extracted with CH_2Cl_2 (300 mL). The combined organic phases were evaporated affording 24.370 g of a sticky brown solid that was purified by chromatography (SiO_2 CH_2Cl_2) affording 6.00 g of the product as an *E*/*Z* mixture of isomers as a yellow viscous oil. The *E*/*Z* ratio was determined to be 1:4 (by GC-MS). ^{1}H NMR ($CDCl_3$) (*E* isomer) δ 7.75 (d, *J* = 3.3 Hz, 1H), 7.36 (d, *J* = 15.3 Hz, 1H), 7.17 (d, *J* = 3.3 Hz, 1H), 7.03 (d, *J* = 15.9 Hz, 1H), 6.74 (m, 1H), 6.61 (m, 1H), 6.18 (m, 1H), 3.99 (t, *J* = 7.2 Hz, 2H), 1.76 (quint, *J* = 6.6 Hz, 2H), 1.31 (m broad, 6H), 0.88 (t broad, 3H); ^{13}C NMR ($CDCl_3$) δ 167.8, 143.5, 136.1, 129.8, 124.4, 122.3, 117.5, 117.3, 109.1, 47.5, 31.9, 31.7, 26.8, 22.9, 14.4. Anal. Calcd for $C_{15}H_{20}N_2S$: C, 69.19; H, 7.74; N, 10.76; Found: C, 69.07; H, 7.81; N, 10.83.

2-[2-(1-Hexyl-1H-pyrrol-2-yl)-vinyl]-thiazole pure E isomer (8). Iodine (300 mg) was added in the dark and in small portions directly as a solid to a stirred solution of mixture of isomers **7** (6.000 g, 23.04 mmol) in CH_2Cl_2 (50 mL). After one night at room temperature the yellow solution was diluted with 100 mL of CH_2Cl_2 and washed with 5 % $Na_2S_2O_3$ (100 mL). Organic phase was separated, dried over $MgSO_4$ and evaporated. Chromatographic purification (SiO_2**,** CH_2Cl_2) afforded the pure *E* isomer as a yellow solid (5.63 g, yield 94%).

1-Hexyl-5-(2-thiazol-2-yl-vinyl)-1H-pyrrole-2-carbaldehyde (9). Anhydrous DMF (1.540 g, 21.10 mmol) was added at 0 °C and under nitrogen to freshly distilled $POCl_3$ (3.220 g, 21.00 mmol) and the resulting solution was stirred until complete conversion into a glassy solid that was taken up with anhydrous acetonitrile (15 mL). The resulting colorless solution was added dropwise at 0 °C to a yellow solution of **8** (5.300 g, 20.35 mmol) in anhydrous acetonitrile (100 mL). The solution color turns red. Mixture was stirred at room temperature overnight and diluted with 15 ml of a 10% K_2CO_3 aqueous solution. After 10 min under vigorous stirring the suspension was diluted with 50 ml of water and 100 ml of AcOEt. Organic phase was separated, washed again with 5% K_2CO_3 (3 × 100 ml), dried over $MgSO_4$ and evaporated yielding 5.88 g of a brown yellow solid that was purified by chromatography (SiO_2, CH_2Cl_2) to give the title compound as a yellow oil (5.000 g, yield 85%). ^{1}H NMR ($CDCl_3$) δ 9.52 (s, 1H), 7.83 (d, *J* = 3.0 Hz,

1H), 7.37 (d, *J* = 16.2 Hz, 1H), 7.31 (d, *J* = 3.3 Hz, 1H), 7.27 (d, *J* = 15.9 Hz, 1H), 6.93 (d, *J* = 4.5 Hz, 1H), 6.64 (d, *J* = 3.9 Hz, 1H), 4.47 (t, *J* = 7.8 Hz, 2H), 1.72 (m, 2H), 1.30 (m, 6H), 0.86 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 179.0, 165.9, 144.0, 139.0, 132.9, 125.0, 124.0, 120.2, 119.0, 109.3, 45.4, 31.8, 31.6, 26.5, 22.8, 14.3. Mass (GC/MS) – 288 (100)[M+], 287(96), 259(38), 231(19), 217(20), 203(49), 189(36), 175(50). Anal. Calcd for: $C_{16}H_{20}N_2OS$: C, 66.63; H, 6.99; N, 9.71; Found: C, 66.44; H, 6.96; N, 9.95.

Dibutyl-(4-{2-[1-hexyl-5-(2-thiazol-2-yl-vinyl)-1H-pyrrol-2-yl]-vinyl}-phenyl)-amine (10). A solution of 4-[bis-butylamino]-benzyl diethylphosphonate[2] (6.400 g, 18.00 mmol) in anhydrous THF (100 ml) was cooled under nitrogen at 0 °C and ^{t}BuOK (2.240 g, 20 mmol) was added directly as a solid. After 10 minutes a solution of aldehyde **9** (5.000 g, 17.32mmol) in 100 ml of the same solvent was added dropwise. The solution immediately turns deep orange. After 1.5 h at 0°C a solution of ^{t}BuOK (2.000 g, 17.82 mmol) in THF (20 ml) was added dropwise and the reaction mixture was stirred at 0 °C for 2 additional hours. Solvent was removed under reduced pressure and the red oily residue was taken up with 150 mL of saturated NaCl and extracted with AcOEt (2 × 150 ml). Organic phase was dried over $MgSO_4$ and evaporated yielding 7.70 g of a red oil that was purified by chromatography (first Al_2O_3 AcOEt/Hexane 1:4, then SiO_2 CH_2Cl_2/Hexane 2:1) affording the pure compound as a red very viscous oil (4.500 g, yield 54%). ^{1}H NMR (CD_2Cl_2) δ 7.73 (d, *J* = 3.3 Hz, 1H), 7.37 (d, *J* = 15.6 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 3.3 Hz, 1H), 7.04 (d, *J* = 15.6 Hz, 1H), 6.90 (d, *J* = 15.9 Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.69 (d, *J* = 3.9 Hz, 1H), 6.64 (d, *J* = 8.70 Hz, 2H), 6.51 (d, *J* = 4.2 Hz, 1H), 4.09 (t, *J* = 7.8 Hz, 2H), 3.31 (t, *J* = 7.8 Hz, 4H), 1.74 (quint, *J* = 6.6 Hz, 2H), 1.65-1.53 (m, 4H), 1.45-1.26 (m, 10H), 0.98 (t, *J* = 7.2 Hz, 6H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (CD_2Cl_2) δ 167.8, 147.9, 143.5, 135.9, 130.4, 128.4, 127.4, 124.6, 122.1, 117.0, 116.5, 111.8, 111.6, 109.9, 106.9, 51.0, 43.5, 31.9, 31.8, 29.8, 26.8, 22.9, 20.7, 14.2. Anal. Calcd for: $C_{31}H_{43}N_3S$: C, 76.02; H, 8.85; N, 8.58; Found: C, 75.96; H, 8.78; N, 8.47.

2-(2-{5-[2-(4-Dibutylamino-phenyl)-vinyl]-1-hexyl-1H-pyrrol-2-yl}-vinyl)-thiazole-5-carbaldehyde (11). A solution of ^{n}BuLi (0.67 mL of a 2.5 M hexane solution, 1.68 mmol) in anhydrous THF (2 ml), was added dropwise at –78 °C to a solution of compound **10** (0.410 g, 0.84 mmol) in the same solvent (18 ml). The solution was stirred

at –78°C for 60 minutes, the color slowly turns brown. A solution of anhydrous and freshly distilled N-formylmorpholine (0.15 ml, 1.45 mmol) in anhydrous THF (2 ml) was added dropwise and the solution stirred for 60 min at –78 °C and for 20 min at room temperature. The clear, fluorescent yellow solution was poured into 50 ml of a saturated NH_4Cl solution and stirred at room temperature for 15 minutes. The deep violet organic phase was separated and the aqueous layer was extracted with AcOEt (3 × 20 ml). Combined organic phase was dried over $MgSO_4$ and evaporated yielding a violet oil that was purified by column chromatography (SiO_2, Hexane/AcOEt 3:1) affording the pure title compound as a deep violet oil that over a week crystallizes into a sticky solid (0.200 g, 46%). ^{1}H NMR (CD_2Cl_2) δ 9.94 (s, 1H), 8.29 (s, 1H), 7.59 (d, *J* = 15.3 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 15.6 Hz, 1H), 6.97 (d, *J* = 15.9 Hz, 1H), 6.85 (d, *J* = 4.5 Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 3.9 Hz, 1H), 4.11 (t, *J* = 7.8 Hz, 2H), 3.31 (t, *J* = 7.5 Hz, 4H), 1.75 (quint, *J* = 7.2 Hz, 2H), 1.65-1.52 (m, 4H), 1.45-1.24 (m, 10H), 0.98 (t, *J* = 7.2 Hz, 6H), 0.90 (m, 3H); ^{13}C NMR (CD_2Cl_2) δ 181.6, 175.1, 153.2, 148.2, 138.1, 136.5, 130.2, 130.0, 127.7, 125.8, 124.2, 114.6, 112.7, 111.8, 111.0, 108.0, 51.0, 43.6, 31.9, 31.8, 29.8, 26.8, 22.9, 20.7, 14.2. EI-MS (T = 451 °C) m/z (%) – 517 (100)[M^+], 474 (20), 432 (16), 259 (15), 237 (7). Anal. Calcd for: $C_{32}H_{43}N_3OS$: C, 74.23; H, 8.37; N, 8.12; Found: C, 73.96; H, 8.47; N, 7.91.

2-(3-Cyano-4-{2-[2-(2-{5-[2-(4-dibutylamino-phenyl)-vinyl]-1-hexyl-1H-pyrrol-2-yl}-vinyl)-thiazol-5-yl]-vinyl}-5,5-dimethyl-5H-furan-2-ylidene)-malononitrile (1a). A suspension of aldehyde **11** (0.050 g, 0.1 mmol) and acceptor **2** (0.030 g, 0.15 mmol) in 1 ml of ethanol and a drop of piperidine was heated under microwave in a sealed vessel at a constant power of 90 W for 8 min with a simultaneous cooling (nitrogen 20 psi). Reaction mixture was cooled at 0 °C and filtered affording a golden brown powder that was washed directly on the filter with 10 ml of cold ethanol (0.033 g, 47 %). ^{1}H NMR (CD_2Cl_2) δ 8.05 (s, 1H), 7.79 (d, *J* = 15.9 Hz, 1H), 7.58 (d, *J* = 15.3 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 16.5 Hz, 1H), 7.01 (d, *J* = 15.0 Hz, 1H), 6.89 (d, *J* = 4.2 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.68-6.60 (m, 3 H), 6.55 (d, *J* = 15.9 Hz, 1H), 4.12 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 7.5 Hz, 4H), 1.78 (s, 6H), 1.66-1.53 (m, 2H), 1.45-1.28 (m, 10H), 0.98 (t, *J* = 7.2 Hz, 6H), 0.91 (m, 3H). ^{13}C (CD_2Cl_2) δ 173.7, 173.2, 152.8, 14δ 173.7, 173.2, 152.8, 148.3, 139.4, 136.7, 133.6, 130.9, 130.8, 127.9, 126.0, 125.8, 124.1,

114.6, 114.3, 113.9, 112.4, 111.8, 111.1, 110.6, 108.8, 97.6, 56.3, 51.0, 31.8, 30.0, 29.8, 26.7, 26.6, 22.9, 20.7, 14.2, 14.1. Mass spectrometry-FAB, m/e (relative intensity) 724.2 (100), 681.2 (5), 431.3 (12), 339.2 (14). Anal. Calcd for: $C_{43}H_{48}N_6OS$: C, 74.10; H, 6.94; N, 12.06; Found: C, 73.60; H, 7.20; N, 11.92.

3-[2-(2-{5-[2-(4-Dibutylamino-phenyl)-vinyl]-1-hexyl-1H-pyrrol-2-yl}-vinyl)-thiazol-5-yl]-propenal (12). A solution of ^{n}BuLi (1.47 mL of a 2.5 M hexane solution, 3.68 mmol) in anhydrous THF (4 mL), was added dropwise at –78 °C to a solution of compound **10** (0.900 g, 1.84 mmol) in the same solvent (30 mL). The solution was stirred at –78°C for 60 min, the color slowly turns brown. A solution of freshly distilled dimethylaminoacroleine (0.37 mL, 3.70 mmol) in anhydrous THF (4 mL) was added dropwise and the solution stirred for 60 min at –78 °C and for 60 min at 0 °C. A saturated NH_4Cl solution (50 mL) was poured into the clear, fluorescent yellow solution and the resulting deep red mixture was stirred at room temperature for 20 min. The deep violet organic phase was separated and the aqueous phase was extracted with AcOEt (2 × 20 ml). Combined organic phase was dried over $MgSO_4$ and evaporated yielding a violet oil that was purified by column chromatography (SiO_2, Hexane/AcOEt 3:1) affording the pure title compound as a deep violet solid (0.470 g, 47 %). ^{1}H NMR (CD_2Cl_2) δ 9.61 (d, *J* = 7.8 Hz, 1H), 7.92 (s, 1H), 7.61 (d, *J* = 15.3 Hz, 1H), 7.48 (d, *J* = 15.6 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 15.6 Hz, 1H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.80 (d, *J* = 4.5 Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 3.9 Hz, 1H), 6.36 (dd, *J* = 15.6, 7.8, 1H), 4.11 (t, *J* = 7.8 Hz, 2H), 3.31 (t, *J* = 7.5 Hz, 4H), 1.75 (quint, *J* = 7.2 Hz, 2H), 1.65-1.52 (m, 4H), 1.45-1.24 (m, 10H), 0.98 (t, *J* = 7.2 Hz, 6H), 0.90 (m, 3H); . ^{13}C NMR (CD_2Cl_2) δ 192.2, 171.4, 148.9, 148.1, 141.3, 137.6, 132.4, 130.3, 129.6, 128.7, 127.6, 124.5, 124.4, 115.2, 111.9, 111.8, 111.2, 107.8, 51.0, 43.6, 31.8, 31.7, 29.8, 22.9, 20.7, 14.2. EI-MS (T = 452 °C) m/z (%) – 543 (100)[M^+], 500 (8), 443 (6), 393 (4), 272 (12), 218 (6). Anal. Calcd for: $C_{34}H_{45}N_3OS$: C, 75.09; H, 8.34; N, 7.73; Found: C, 75.00; H, 8.60; N, 7.40.

2-(2-{3-[2-(2-{5-[2-(4-Dibutylamino-phenyl)-vinyl]-1-methyl-1H-pyrrol-2-yl}-vinyl)-thiazol-5-yl]-allylidene}-1,1-dioxo-1,2-dihydro-1λ^6-benzo[b]thiophen-3-ylidene)-malononitrile (1c). A suspension of aldehyde 12 (0.100 mg, 0,184 mmol) and acceptor **3** (0.050 g, 0.217 mmol) in ethanol (35 mL) was refluxed for 3 h. The resulting violet

suspension was hot filtered and the dark violet precipitate was washed directly on the filter with 50 ml of boiling ethanol. Crystallization form CH_2Cl_2/EtOH (1:1) afforded the pure compound as a violet shiny solid (60 mg, yield 48%). ^{1}H NMR (CD_2Cl_2) δ 8.83 (d, *J* = 7.4 Hz, 1H), 8.48 (d, *J* = 12.1 Hz, 1H), 8.01 (s, 1H), 7.98 (m, 1H), 7.89 (td, *J* = 7.1, 1.2 Hz, 1H), 7.84 (td, *J* = 7.3, 1.6 Hz, 1H), 7.51 (d, *J* = 15.4 Hz, 1H), 7.50 (d, *J* = 14.2 Hz, 1H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.31 (dd, *J*= 12.0, 14.3 Hz, 1H), 6.99 (d, *J* = 15.3 Hz, 2H), 6.88 (d, *J* = 4.4 Hz, 1H), 6.71 (d, *J* = 15.8 Hz, 1H), 6.60 (d, *J* = 4.5 Hz, 1H), 6.60 (d, *J* = 14.4 Hz, 1H), 4.12 (t, *J* = 7.7 Hz, 2H), 3.32 (t, *J* = 6.6 Hz, 4H), 1.76 (q, *J* = 6.9 Hz, 2H), 1.67-1.21 (m, 14H), 1.01-0.80 (m, 9H); Mass spectrometry-FAB, m/e (relative intensity) 755.1 (100), 699.1 (8), 543.2 (20), 392.2 (43). Anal. Calcd for: $C_{40}H_{39}N_5O_2S_2$: C, 71.49; H, 6.53; N, 9.26; Found: C, 71.32; H, 6.65; N, 9.24.

2-(3-Cyano-4-{4-[2-(2-{5-[2-(4-dibutylamino-phenyl)-vinyl]-1-hexyl-1H-pyrrol-2-yl}-vinyl)-thiazol-5-yl]-buta-1,3-dienyl}-5,5-dimethyl-5H-furan-2-ylidene)-malononitrile (1b). Aldehyde **12** (0.15 g, 0.28 mmol) and acceptor **2** (0.07 g, 0.35 mmol) were dissolved in a solution of EtOH (3 mL), $AcONH_4$ (2.5 mg) and AcOH (3.8 mg). The violet mixture was refluxed for 2 h, color turns dark brown. After cooling at room temperature, mixture was filtered affording a dark precipitate that was washed directly on the filter with EtOH (10 mL) and then crystallized form ethanol to give the pure compound as a dark powder (0.13 g, yield 64%). ^{1}H NMR (CD_2Cl_2) δ 7.86 (s, 1H), 7.51 (dd, *J* = 11.7, 14.8 Hz, 1H), 7.49 (d, *J* = 15.4 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 14.9 Hz, 1H), 6.99 (d, *J* = 15.4 Hz, 1H), 6.97 (d, *J* = 15.9 Hz, 1H), 6.83 (d, *J* = 4.3 Hz, 1H), 6.75 (d, *J* = 15.4 Hz, 1H), 6.73 (d, *J* = 14.8 Hz, 1H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 4.3 Hz, 1H), 6.53 (d, *J* = 15.4 Hz, 1H), 4.11 (t, *J* = 7.3 Hz, 2H), 3.32 (t, *J* = 7.8 Hz, 4H), 1.81-1.69 (m, 2H), 1.65-1.50 (m, 8H), 1.45-1.29 (m, 10H), 0.98 (t, *J* = 7.3 Hz, 6H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (CD_2Cl_2) δ 173.4, 170.9, 149.0, 148.2, 147.4, 138.1, 135.5, 135.4, 134.5, 128.4, 127.7, 124.5, 124.3, 117.8, 115.2, 112.5, 111.8, 111.1, 111.0, 108.1, 97.8, 97.7, 51.0, 43.6, 31.8, 29.8, 26.8, 26.5, 22.9, 20.7, 14.1. Mass spectrometry-FAB, m/e (relative intensity) 724.2 (100), 681.2 (5), 431.3 (12), 339.2 (14). Anal. Calcd for: $C_{45}H_{52}N_6OS$: C, 74.55; H, 7.23; N, 11.59; Found: C, 74.21; H, 7.38 N, 11.19.

Table S1. Absorption maxima in nm (ε_{max} in 10^3 $M^{-1}cm^{-1}$) for the low-energy bands of chromophores **1a-c** in various solvents.

	THF	CH_2Cl_2	benzene	DMF
1a	718 (57.0)	751	731	725
1b	691 (38.4)	722	722	693
1c	812 (46.4)	850 (42.2)	832	841

Table S2. Half-wave potentials ($E_{1/2}$ vs. $FeCp_2^{+/0}$ in V) for chromophores **1a**,**1b** and **1c** in CH_2Cl_2 / 0.1 M $[^nBu_4N]^+[PF_6]^-$.

	$E_{1/2}(M^{2+/+})$	$E_{1/2}(M^{+/0})$	$E_{1/2}(M^{0/-})$
1a	+0.22	–0.03	–1.00
1b	+0.21	–0.06	–0.95
1c	+0.27	–0.01	–0.78

3. Details for the Two-Photon Measurements and Preliminary Data for 1b and 1c

The femtosecond laser used is a Ti:Sapphire-based CPA-2001 system (CLARK-MXR) which provides laser pulses at 775nm of 140fs (FW1/eM of intensity) duration, with an energy of 0.94mJ/pulse at a 1 KHz repetition rate. The laser pumps two optical parametric amplifier systems (TOPAS, Light Conversion), tunable over a broad range from visible to near-infared. 2-3 μJ of 1300 nm light from TOPAS2 is focused tightly into a 2.5mm-thick piece of calcium fluoride (CaF_2) for generation of the probe white-light continuum (WLC) pulse. Pump and WLC-probe overlap at the sample in both space and time. Prior to arriving on the sample, a fraction of WLC-probe is sampled by a broadband 50/50 beam splitter as reference in order to monitor fluctuations in the probe beam. Both WLC-probe reference and signal are sent into a dual-fiber input spectrometer (Spectro150, Acton Research), which is coupled to a dual diode array (Princeton Instruments Silicon DPDA 2048).

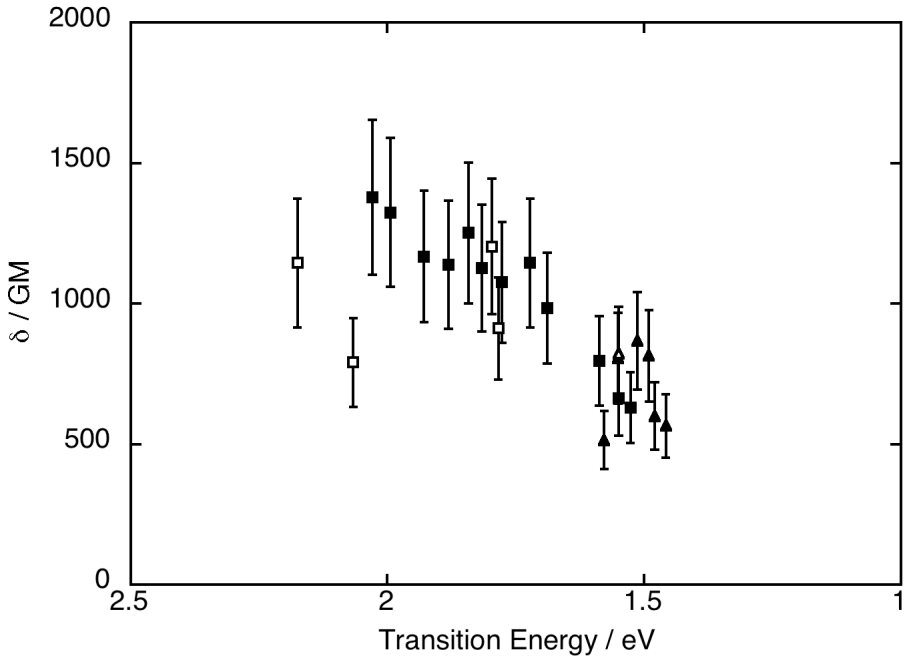


Figure S1. Preliminary 2PA data for **1b** (squares) and **1c** (triangles) in THF and CH2Cl2 respectively (**1c** was insufficiently soluble in THF). Filled symbols are pump-probe data (λ_{pump} = 1800 nm for **1b**, 1900 nm for **1c**) and open symbols are Z-scan data.

4. Computational Methodology

The geometry optimization was performed at the semi-empirical Hartree-Fock (HF) Austin Model 1 (AM1)[3] method. All molecules are studied in their all-transoid configurations (shown in Scheme 1 of the paper). On the basis of the AM1 geometries, the electronic properties (dipole moments, transition dipole moments and transition energies) are evaluated using the semi-empirical Intermediate Neglect of Differential Overlap (INDO) Hamiltonian,[4] as implemented in the ZINDO code. The spectroscopic parametrization, along with the Mataga-Nishimoto electron repulsion scheme,[5] is used. The INDO calculation is coupled to a Multi-Reference Determinants Configuration Interaction (MRDCI) scheme, for which the excitations are taken among the 6 highest occupied and 6 lowest unoccupied π-molecular orbitals. Five reference determinants are considered: SCF, H→L, H-2→L, H-1→L, H-1→L+1 (H is the HOMO {Highest Occupied Molecular Orbital} and L the LUMO {Lowest Unoccupied Molecular Orbital}) and SCF refers to the self-consistent field determinant).The two-photon absorption (2PA) cross sections are calculated using the Sum-Over-States (SOS) method[6] including the first 300 singlet excited states.

To obtain non-degenerate two-photon absorption cross-sections we follow the approach outlined in reference 7, where a good agreement between theoretical and experimental values of non-degenerate 2PA cross-sections has been found.

The non-degenerate and degenerate cross-sections are compared in Table 1 of the paper. When using the actual photon energy of the pump beam used for **1a** (0.689 eV, corresponding to 1800 nm) huge pre-resonance enhancement effects are obtained (see second line in Table S2). This overestimation of the non-degenerate cross-sections is is caused by the overestimation of the transition energies by the INDO method (compare Tables 1 and Figure 2 in the main paper, Table S1). In order to overcome this problem, we calculated non-degenerate 2PA cross-sections using a "scaled pump" energy. Here the *ratios* of the pump, probe and transition energies are adjusted to the experimental values (rather than using a fixed pump energy). In this case, the energies of the pump beam photons are set to 0.971 eV, 0.948 eV and 1.066 eV for chromophores **1a-c** respectively. This provides a much more realistic estimate of the pre-resonance enhancement (see third line in Table S2), especially, as within the often-applied two-state model, the pre-

resonance enhancement is determined by the ratio between the probe photon energy and the transition energy.[8,9]

Table S3. Degenerate and non-degenerate 2PA cross-sections in GM for chromophores **1a-c** using the INDO/MRDCI method (with a 6*6 CI space and five determinants), using the unscaled experimental pump energy and a pump energy scaled as described in the text.

	1a	**1b**	**1c**
δ_{deg}	752	1070	904
Unscaled $\delta_{non\text{-}deg}$	2565	3791	2825
scaled $\delta_{non\text{-}deg}$	1224	1888	1113

5. References for Supplementary Information

(1) Procedure adapted from: Kim, I. T.; Elsenbaumer, R. L *Tetrahedron Lett* **1998**, *39*, 1087.

(2) Marder, S. R.; Perry, J.; Zhou, W.; Kuebler, S. M.; Cammack, J. K. "Materials, methods, and uses for photochemical generation of acids and/or radical species" PCT Int. Appl. WO 2002079691, **2002**, 181 pp.

(3) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P., *J. Am. Chem. Soc.* **1985,** *107*, 3902.

(4) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A., *J. Chem. Phys.* **1967,** *47*, 2026.

(5) Mataga, N.; Nishimoto, K., *Z. Phys. Chem.* **1957,** *13*, 140.

(6) Orr, B. J.; Ward, J. F., *Mol. Phys.* **1971,** *20*, 513.

(7) Hales, J. M.; Hagan, D. J.; Van Stryland, E. W.; Schafer, K. J.; Morales, A. R.; Belfield, K. D.; Pacher, P.; Kwon, O.; Zojer, E.; Brédas, J. L., *J. Chem. Phys.* **2004,** *121*, 3152-3160.

(8) Pacher, P. Diploma Thesis, Graz University of Technology, **2003**.

(9) In the present molecules, the two state model somewhat overestimates the degenerate 2PA cross-sections. This shortcoming, however, is strongly reduced for non-degenerate 2PA, where the channel related to the two-state description is strongly emphasized by the pre-resonance enhancement. (compare also reference 7).