Supplementary Material

Degenerate two-/three-photon absorption and optical power limiting properties in femtosecond regime of a multi-branched chromophore

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Materials

All commercially available reagents for the preparation of the intermediates and targeted chromophore including triphenylamine, tetrabutylammonium tribromide ($TBABr_3$), triphenylphosphine ($P(C_6H_5)_3$), *p*-toluic hydrazide, 4-*tert*-butyl benzoyl chloride, 1-bromohexane, fluorene, paraformaldehyde, 33% wt HBr (in acetic acid solution), phosphorus oxychloride ($POCl_3$), *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), carbon tetrachloride (CCl_4), sodium hydroxide, sodium hydride (NaH, 60% dispersion in mineral oil), palladium(II) acetate ($Pd(OAc)_2$), tri-*o*-tolylphosphine ($P(o\text{-tolyl})_3$), triethylamine, and acetonitrile were obtained from Aldrich Chemical Co. and were used as received, unless stated otherwise.

Measurements

^{1}H-NMR spectra were carried out at 400 MHz. Elementary analysis was performed by Atlantic Microlab, Inc., Norcross, GA. High-resolution mass spectroscopy (HRMS) was conducted by using VG Analytical 70-SE/11-250J mass spectrometer.

Synthesis

In Scheme 1, compounds **1**, **2**, **3** and **5** were synthesized by following the established literature processes[1-4] and obtained with the overall yields of 88 % for compound **1**, 90 % for compound **2**, ~45 % for compound **3**, and ~65 % for compounds **5**. For the synthesis of compounds **4** and **6**, the well-known Heck and Wittig coupling reactions[5,6] have been followed and these two compounds were obtained with the yields of 70% and 72%, respectively. The experimental details for the preparation and characterization of compounds **4** and **6** are presented as the following:

4-{Bis[4-(4-(5-(4--*tert*-butylphenyl)-[1,3,4]-oxadiazol-2-yl)styryl)phenyl]amino}-benzaldehyde (Compound 4)

Compound **2** (1.0 equiv.), compound **3** (2.1 equiv.), $Pd(OAc)_2$ (0.04 equiv.), P(*o*-tolyl)$_3$ (0.24 equiv.), triethylamine (~5mL) and acetonitrile (~15mL) was added to a heavy-wall pressure tube equipped with a magnetic stirrer and a rigid Teflon cap. The reaction mixture was then heated up to 110 °C under nitrogen atmosphere and kept at this temperature by means of a heating mantle for 18 hours. After cooling, the reaction mixture was poured into methanol. The crude product was filtered off and purified by column chromatography on silica gel using ethyl acetate-hexane (1:5) as the eluent to afford the title compound as bright yellow powder in ~70% yield. ^{1}H-NMR (400 MHz; $CDCl_3$, ppm,): δ 9.81 (s, 1H), 8.11 (d, 4H, *J* = 8.0 Hz), 8.05 (d, 4H, *J* = 8.0 Hz), 7.72 (d, 4H, *J* = 8.0 Hz), 7.69 (d, 2H), 7.57 (d, 4H, *J* = 8.0 Hz), 7.47 (d, 4H), 7.25 (d, 2H, *J* = 16.0 Hz), 7.15 (d, 4H), 7.09 (d, 2H, *J* = 16.0 Hz), 7.03 (d, 2H), 1.38 (s, 18H); HRMS (EI, 70 eV): calcd for M^+ 877.3992, found 877.3981; Anal. Calcd. For $C_{59}H_{51}N_5O_3$: C, 80.70; H, 5.85; N, 7.98. Found: C, 80.79; H, 5.77; N, 8.10.

[2,7-Di{4-[bis(4-(4-(5-(4-*tert*-butylphenyl)-[1,3,4]-oxadizol-2-yl)styryl)phenyl)amino)styryl]}-9,9-dihexylfluorene (Compound 6)

To a solution of compound **5** (1.0 equiv.) and sodium hydride (3.5 equiv) in THF (~30mL) was added compound **4** (2.1 equiv.) gradually at room temperature under N_2 atmosphere. The resulting mixture was heated to reflux for 24 hours and then cooled to room temperature. The reaction mixture was poured into 50mL methanol with vigorous stirring. The precipitate formed was collected and washed thoroughly with methanol. The crude product was then purified through column chromatography on silica gel by using ethyl acetate-hexane (1:7) as the eluent to afford yellow powder in 72% yield. ^{1}H-NMR (400 MHz; $CDCl_3$, ppm, tentative assignment): δ 8.12 (d, 8H, *J* = 8.0 Hz), 8.06 (d, 8H, *J* = 8.0 Hz), 7.72 (d, 8H, *J* = 8.0 Hz), 7.61 (d, 8H, *J* = 8.0 Hz), 7.54 (m, 4H), 7.46 (m, 12H), 7.42 (s, 2H), 7.28 (d, 2H, *J* = 15.6 Hz), 7.20 (d, 4H, *J* = 16.0 Hz), 7.14 (m, 12H), 7.10 (d, 2H, *J* = 15.6 Hz), 7.06 (d, 4H, *J* = 16.0 Hz), 2.04 (t, 4H), 1.37 (s, 36H), 1.08 (bm, 12H), 0.83 (t, 6H), 0.57 (m, 4H); HRMS (FAB): calcd for M^+ 2081.0746, found 2081.0708; Anal. Calcd. For $C_{145}H_{136}N_{10}O_4$: C, 83.62; H, 6.58; N, 6.73. Found: C, 83.55; H, 6.76; N, 6.67.

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