Supplementary Material

Degenerate Nonlinear Absorption and Optical Power Limiting Properties of Asymmetrically Substituted Stilbenoid Chromophores

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Materials

All commercially available reagents for the preparation of the intermediates and model chromophores including triphenylamine, tetrabutylammonium tribromide ($TBABr_3$), *p*-toluenesulfinic acid–sodium salt hydrate, ploy(ethylene glycol) (PEG-400), bromoethane, 4-nitrobenzyl bromide, triphenylphosphine ($P(C_6H_5)_3$), *p*-toluic hydrazide, 4-*tert*-butyl benzoyl chloride, phosphorus oxychloride ($POCl_3$), *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), carbon tetrachloride (CCl_4), *o*-Aminothiophenol, *p*-toluoyl chloride, 1-methyl-2-pyrrolidinone (NMP), styrene, brombenzene, palladium(II) acetate ($Pd(OAc)_2$), tri-*o*-tolylphosphine, triethylamine, acetonitrile, styrene, and bromobenzene were obtained from Aldrich Chemical Co. and were used as received, unless stated otherwise.

Measurements

^{1}H-NMR spectra were carried out at 300 or 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** to **5** were synthesized by using established literature processes[1-3] and obtained with the yields of 90 % for compound **1**, 85 % for compound **2**, 65 % for compound **3**, and ~80 % for compounds **4** and **5**. The synthesis of the intermediates with oxadiazole (compounds **6**, **7** and **8**) and benzothiazole (compounds **9**, **10** and **11**) functional groups shown in Scheme 2 were carried out by following the literature procedures[4,5] and were obtained in overall yields of ~45 % for compound **8** and ~50 % for compound **11**. For the final coupling reactions, the well-known Heck reaction has been followed to prepare the selected model chromophores **Dor**, **Acc**, **S101**, **101**, **BT101** and **N101** as shown in Scheme 3. The details for the preparation and characterization of these model compounds are presented as the following:

General synthetic procedure for Heck coupling reaction[6]

Aryl bromide (1.0 equiv.), vinylated aryl compounds (1.1 equiv.), tri-*o*-tolylphosphine (TOP, 0.12 equiv.), palladium(II) acetate (0.02 equiv.) and triethylamine (20 ml) were added to a heavy-wall high pressure reaction tube equipped with a magnetic stirrer and a rigid Teflon cap. The reaction mixture was heated up to 110 °C under nitrogen atmosphere and kept at this temperature by means of an oil bath or a heating mantle for

15 hours. After cooling, the reaction mixture was poured into 200ml methanol. The crude product was filtered off and purified either by column chromatography or recrystallization.

Diphenyl-(4-styryl-phenyl)amine (Dor)
4-Bromo-*N*,*N*-diphenylaniline (compound **1**, 1.0 equiv.) and styrene (1.0 equiv.) were used as the starting reagents for the preparation of this model chromophore. Following the standard Heck coupling procedure mentioned above (reaction time: 12 hours), the final product (white-yellow powder) was obtained in 70 % yield after recrystallization form acetone. ^{1}H-NMR (400 MHz; $CDCl_3$, ppm): δ 7.56 (d, 2H, *J* = 7.8 Hz), 7.43 (d, 2H, *J* = 7.8 Hz), 7.40 (d, 2H, *J* = 8.0 Hz), 7.33 (d, 1H, *J* = 16 Hz), 7.20 (d, 2H, *J* = 8.0Hz), 7.17 (m, 1H), 7.15 (d, 1H, *J* = 16 Hz), 7.13 (d, 4H, *J* = 8.4 Hz), 7.10 (d, 6H, *J* = 8.4 Hz); HRMS (EI, 70 eV): calcd for M^+ 347.1674, found 347.1669; Anal. Calcd. For $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03. Found: C, 89.82; H, 6.15; N, 4.05.

2-(4-Styryl-phenyl)-benzothiazole (Acc)
2-(4-Vinyl-phenyl)-benzothiazole (compound **11**, 1.0 equiv.) and bromobenzene (1.0 equiv.) were used as starting materials for the preparation of this model compound. Following the standard Heck coupling procedure (reaction time: 12 hours), the final product (pale-yellow powder) was obtained in 72.5 % yield after column chromatographic purification method on silica gel using ethyl acetate-hexane (1:4) as the eluent. ^{1}H-NMR (400 MHz; $CDCl_3$, ppm): δ 8.16 (d, 1H, *J* = 8.0 Hz), 8.14 (d, 2H, *J* = 8.0 Hz), 7.98 (d, 1H, *J* = 7.6 Hz), 7.71 (d, 2H, *J* = 8.0 Hz), 7.62 (d, 1H, *J* = 8.0 Hz), 7.58 (m, 1H, *J* = 8.0 Hz), 7.47 (m, 1H, *J* = 7.6 Hz), 7.45 (d, 2H, *J* = 8.0 Hz), 7.37 (d, 1H, *J* = 16 Hz), 7.28 (m, 1H, *J* = 8.0 Hz), 7.20 (d, 1H, *J* = 16Hz); HRMS (EI, 70 eV): calcd for M^+ 313.0925, found 313.0910; Anal. Calcd. For $C_{21}H_{15}NS$: C, 80.44; H, 4.82; N, 4.47. Found: C, 80.44; H, 4.86; N, 4.42.

{4-[2-(4-Ethanesulfonyl-phenyl)-vinyl]-phenyl}-diphenylamine (S101)
Starting materials: compound **1** (1.0 equiv.) and compound **4** (1.1 equiv.). Reaction time: 18 hours under N_2. Purification method: column chromatography; eluent: ethyl acetate: hexane = 1:6. Yield: 62 %. Bright yellow solid product. ^{1}H-NMR (300 MHz; $CDCl_3$, ppm): δ 7.84 (d, 2H, *J* = 7.8 Hz), 7.62 (d, 2H, *J* = 7.8 Hz), 7.39 (d, 2H, *J* = 7.8 Hz), 7.28 (d, 2H, *J* = 7.8 Hz), 7.21 (d, 1H, *J* = 16 Hz), 7.15 (d, 1H, *J* = 16 Hz) 7.11 (m, 4H), 7.04 (m, 6H), 3.11 (q, 2H, $-SO_2CH_2CH_3$, *J* = 6.9 Hz), 1.28 (t, 3H, $-SO_2CH_2CH_3$, *J* = 6.9 Hz); HRMS (EI, 70 eV): calcd for M^+ 439.1606, found 439.1609; Anal. Calcd. For $C_{28}H_{25}NO_2S$: C, 76.51; H, 5.73; N, 3.19. Found: C, 76.26; H, 5.71; N, 3.17.

[4-(2-{4-[5-(4-*t*-Butyl-phenyl)-[1,3,4]oxadiazol-2-yl]-phenyl}-vinyl)-phenyl]-diphenylamine (101)
Using compound **1** (1.0 equiv.) and compound **8** (1.1 equiv.) as the starting materials and following the standard procedure of Heck reaction (reaction time: 12 hours) for the synthesis of this chromophore. The yellow solid was then recrystalized from methanol to afford bright yellow crystal product in 63% yield. ^{1}H-NMR (400 MHz; $CDCl_3$, ppm): δ 8.12 (d, 2H, *J* = 8.0 Hz), 8.05 (d, 2H, *J* = 8.0 Hz), 7.70 (d, 2H, *J* = 8.0 Hz), 7.60 (d, 2H, *J* = 8.0 Hz), 7.48 (d, 2H, *J* = 8.0 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 7.25 (d, 1H, *J* = 16 Hz), 7.20

(m, 4H), 7.13 (m, 6H), 7.07 (d, 1H, *J* = 16 Hz), 1.372 (s, 9H); HRMS (EI, 70 eV): calcd for M^+ 547.2624, found 547.2616; Anal. Calcd. For $C_{38}H_{33}NO$: C, 83.33; H, 6.07; N, 7.67. Found: C, 83.63; H, 6.05; N, 7.54.

{4-[2-(4-Benzothiazol-2-yl-phenyl)-vinyl]-phenyl}-diphenylamine (BT101)
Starting materials: compound **1** (1.0 equiv.) and compound **11** (1.2 equiv.). Reaction time: 18 hours under N_2. Purification method: column chromatography; eluent: ethyl acetate: hexane = 1:6. Yield: 66 %. Yellow solid. ^{1}H-NMR (300 MHz; $CDCl_3$, ppm, tentative assignment): δ 8.10 (d, 1H, *J* = 8.0 Hz), 8.07 (d, 2H, *J* = 8.0 Hz), 7.92 (d, 1H, *J* = 8.0 Hz), 7.61 (d, 2H, *J* = 8.0 Hz), 7.49 (d, 2H, *J* = 8.0 Hz), 7.42 (d, 1H, *J* = 8.0 Hz), 7.38 (d, 1H, *J* = 8.0 Hz), 7.30 (m, 4H), 7.21 (d, 1H, *J* = 16 Hz), 7.13 (m, 4H, *J* = 8.0 Hz), 7.07 (m, 4H, *J* = 8.0 Hz), 7.03 (d, 1H, *J* = 16 Hz); HRMS (EI, 70 eV): calcd for M^+ 480.1660, found 480.1637; Anal. Calcd. For $C_{33}H_{24}N_2S$: C, 82.47; H, 5.03; N, 5.83. Found: C, 82.24; H, 5.09; N, 5.69.

{4-[2-(4-Nitro-phenyl)-vinyl]-phenyl}-diphenylamine (N101)
Starting materials: compound **1** (1.0 equiv.) and compound **5** (1.2 equiv.). Reaction time: 17 hours under N_2. Purification method: column chromatography; eluent: ethyl acetate: hexane = 1:5. Yield: 58 %. Red powder product. ^{1}H-NMR (400 MHz; $CDCl_3$, ppm): δ 8.24 (d, 2H, *J* = 8.0 Hz), 7.66 (d, 2H, *J* = 8.0 Hz), 7.48 (d, 2H, *J* = 8.0 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 7.26 (d, 1H, *J* = 16 Hz), 7.20 (m, 4H), 7.09 (m, 6H), 7.11 (d, 1H, *J* = 16 Hz); HRMS (EI, 70 eV): calcd for M^+ 392.1525, found 392.1521; Anal. Calcd. For $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14. Found: C, 79.47; H, 5.30; N, 7.14.

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