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 (TBABr₃), p-toluenesulfonic acid–sodium salt hydrate, poly(ethylene glycol) (PEG-400), bromoethane, 4-nitrobenezyl bromide, triphenylphosphine (PC₆H₅)₃, p-toluic hydrazide, 4-tert-butyl benzoyl chloride, phosphorus oxychloride (POCl₃), N-bromosuccinimide (NBS), benzoyl peroxide (BPO), carbon tetrachloride (CCl₄), o-Aminothiophenol, p-toluoyl chloride, 1-methyl-2-pyrrolidinone (NMP), styrene, bromobenzene, 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
¹H-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): \(\delta \) 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, \(J = 8.0 \) Hz), 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): \(\delta \) 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), 7.58 (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), 7.30 (m, 1H, \(J = 8.0 \) Hz), 7.20 (d, 1H, \(J = 16 \) Hz); 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 (1:4) as the eluent. \(^1\)H-NMR (300 MHz; CDCl\(_3\), ppm): \(\delta \) 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, \(-\text{SO}_2\text{CH}_2\text{CH}_3\), \(J = 6.9 \) Hz), 1.28 (t, 3H, \(-\text{SO}_2\text{CH}_2\text{CH}_3\), \(J = 6.9 \) Hz); HRMS (EI, 70 eV): calcd for M\(^+\) 439.1606, found 439.1609; Anal. Calcd. For C\(_{28}\)H\(_{25}\)NO\(_2\)S: 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): \(\delta \) 8.12 (d, 2H, \(J = 8.0 \) Hz), 8.05 (d, 2H, \(J = 8.0 \) Hz), 7.70 (d, 2H, \(J = 8.0 \) Hz), 7.48 (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 C₃₈H₃₃NO: 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)

{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 N₂. Purification method: column chromatography; eluent: ethyl acetate: hexane = 1:5. Yield: 58 %. Red powder product. ¹H-NMR (400 MHz; CDCl₃, 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 C₂₆H₂₀N₂O₂: C, 79.57; H, 5.14; N, 7.14. Found: C, 79.47; H, 5.30; N, 7.14.

References