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Supporting Information

Femtosecond Spectroscopy and Nonlinear Optical Properties of aza-BODIPY Derivatives in Solution

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1. Synthetic details

Synthesis compound 2 Aza-bodipy **1** (200 mg, 0.204 mmol, 1 equiv.) was dissolved in a DCM/TFA 10:1 mixture (33 mL). NBS (80 mg, 0.449 mmol, 2.2 equiv.) was then added. After stirring at rt for 1 hour, the reaction mixture was neutralized with NaHCO₃, washed with sodium thiosulfate, water, brine and dried over sodium sulfate. The solvent was evaporated under reduced pressure to give the desired compound (126 mg, 54%). An additional purification by flash chromatography is also possible using DCM/Et₃N (99:1) as eluent. ¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.91 (m, 6H), 7.60 (d, *J* = 6.1 Hz, 2H), 7.51 – 7.45 (m, 2H), 6.68 (d, *J* = 9.2 Hz, 4H), 3.33 (t, *J* = 7.6 Hz, 8H), 1.69 – 1.58 (m, 8H), 1.41 – 1.30 (m, 24H), 0.97 – 0.88 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 155.65, 155.15, 153.09, 150.42, 144.87, 138.38, 133.48, 132.19, 128.91, 125.33, 122.14, 116.46, 110.67, 51.28, 31.85, 31.82, 27.51, 26.97, 22.85, 14.20. (One carbon signal is missing). ¹¹B NMR (96 MHz, CDCl₃) δ 0.83 (t, *J* = 29.7 Hz). HRMS (ESI⁺) calcd. for [M+H]⁺: 1136.3383. Found: 1136.3380.

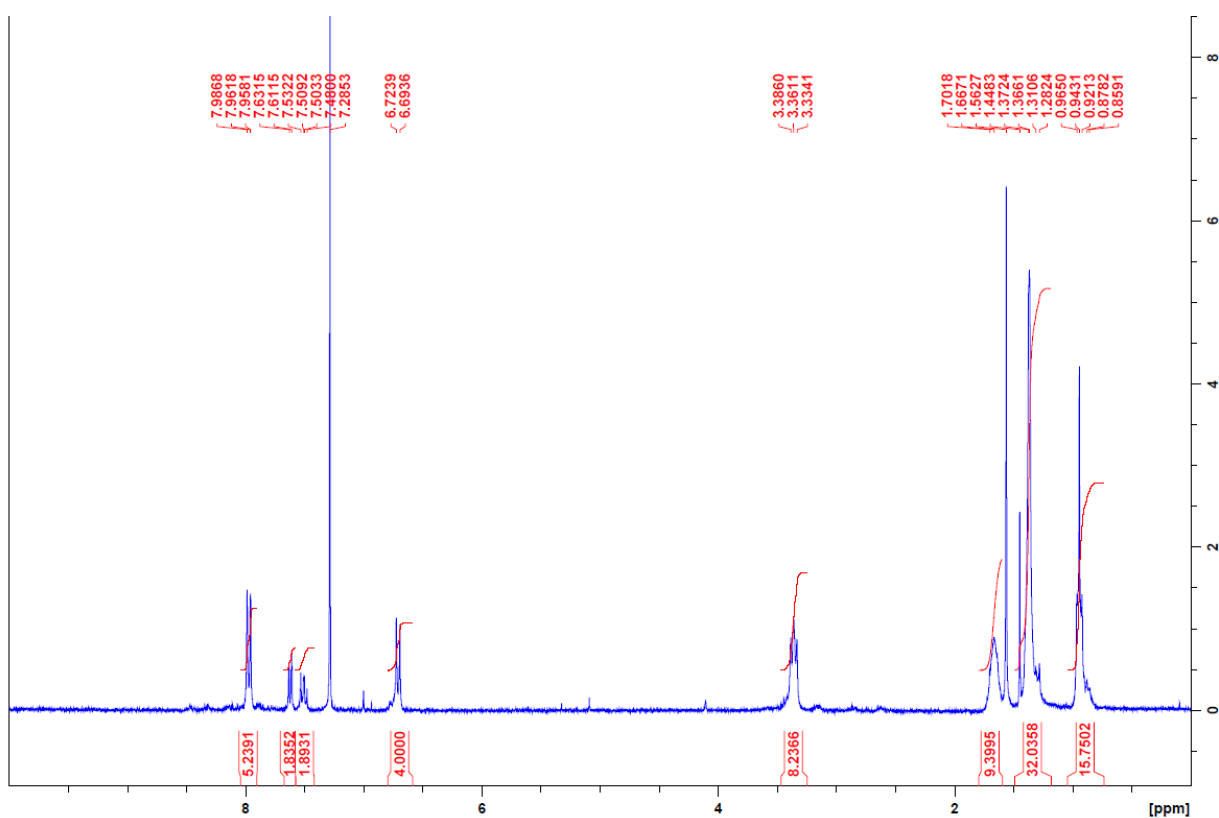


Figure 1. ¹H NMR (400 MHz, CDCl₃) spectrum of **2**.

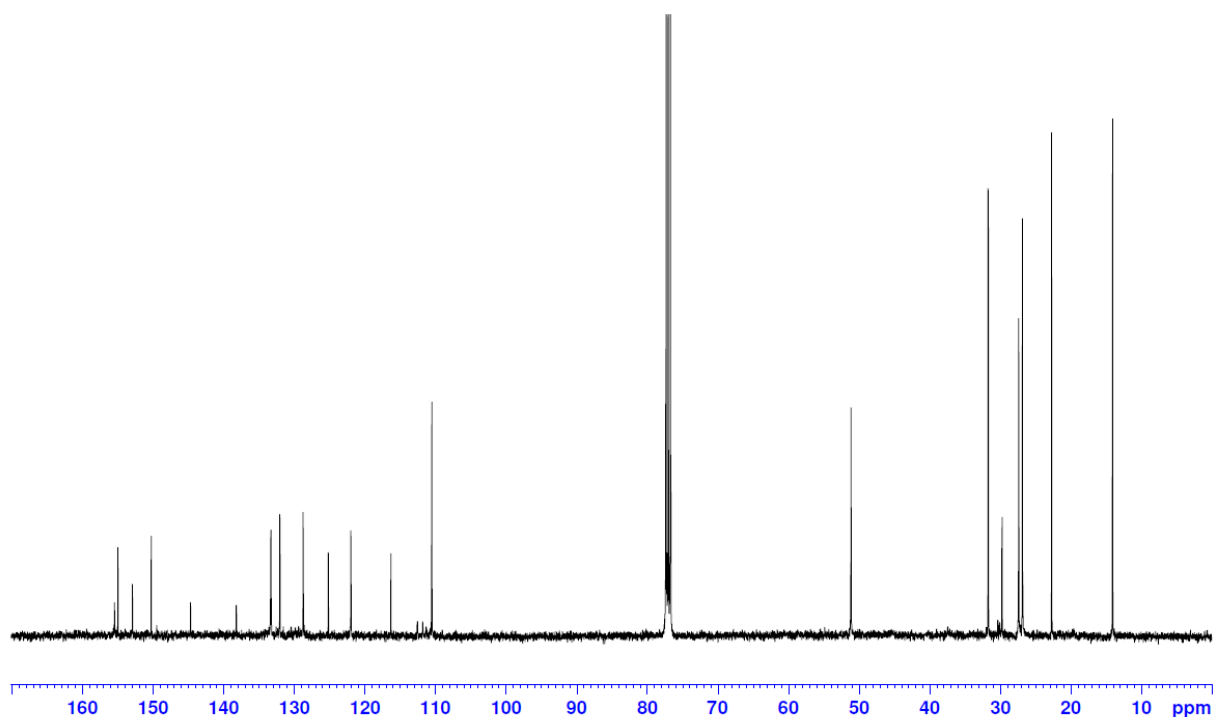


Figure 2. ^{13}C NMR (101 MHz, CDCl_3) spectrum of **2**.

Synthesis compound 4 Aza-bodipy **3** (195 mg, 0.126 mmol, 1 equiv.) was dissolved in a DCM/TFA 10:1 mixture (27.5 mL). Tetrabutylammonium tribromide (122 mg, 0.252 mmol, 2 equiv.) was then added portionwise. The purple reaction mixture quickly turned blue. After 30 min, the reaction was stopped, washed with sat. NaHCO_3 , water, dried over sodium sulfate and evaporated under reduced pressure. The crude was purified by flash chromatography using DCM/EP 1:2 as eluent. The desired product was obtained as a purple-blue film (155 mg, 0.091 mmol, 72%). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.9$ Hz, 4H), 7.72 (d, $J = 8.4$ Hz, 4H), 7.55 (d, $J = 8.5$ Hz, 4H), 7.36 (d, $J = 8.9$ Hz, 4H), 6.98 (d, $J = 8.9$ Hz, 4H), 6.57 (d, $J = 9.0$ Hz, 4H), 3.91 (d, $J = 5.6$ Hz, 4H), 3.27 (t, $J = 7.4$ Hz, 8H), 1.87 – 1.78 (m, 2H), 1.62 – 1.55 (m, 8H), 1.47 – 1.25 (m, 72H), 0.94 – 0.85 (m, 24H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.00, 157.16, 148.27, 144.48, 142.52, 133.26, 132.58, 130.76, 130.60, 128.38, 127.22, 123.33, 114.35, 111.32, 108.60, 94.13, 87.56, 71.22, 51.14, 38.11, 32.07, 32.02, 31.85, 31.50, 30.21, 29.86, 29.77, 29.52, 27.34, 27.02, 26.96,

2. Z-scan results

The results on Z-scan open aperture (OA) measurements for compounds **1-4** in DCM are presented in Figures 5-8 for selected excitation wavelengths.

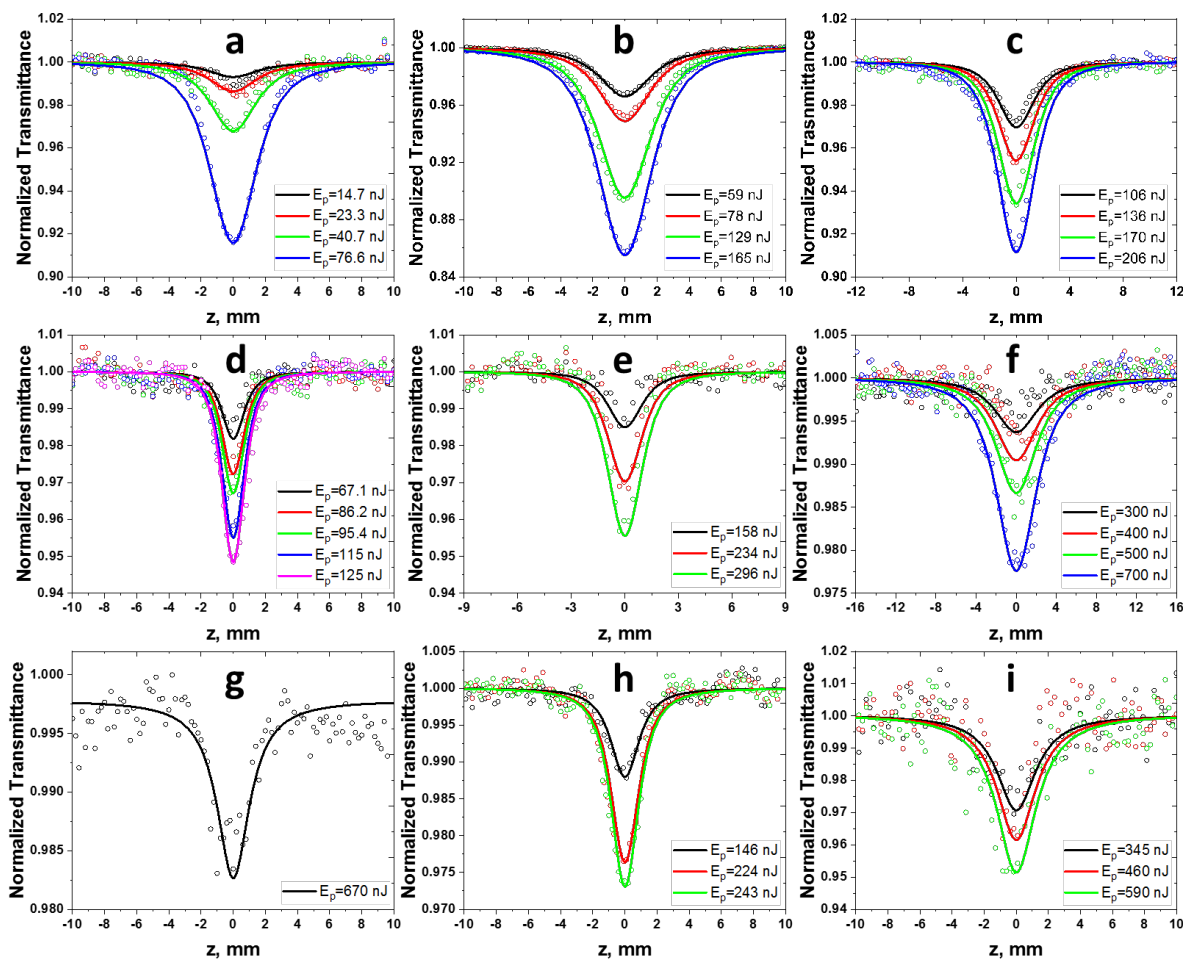


Figure 5. Open aperture Z-scan (circles) and fitting curves (solid lines) for **1** in DCM at (a) 1150 nm, (b) 1200 nm, (c) 1250 nm, (d) 1300 nm, (e) 1350 nm, (f) 1400 nm, (g) 1500 nm, (h) 1550 nm, and (i) 1700 nm.

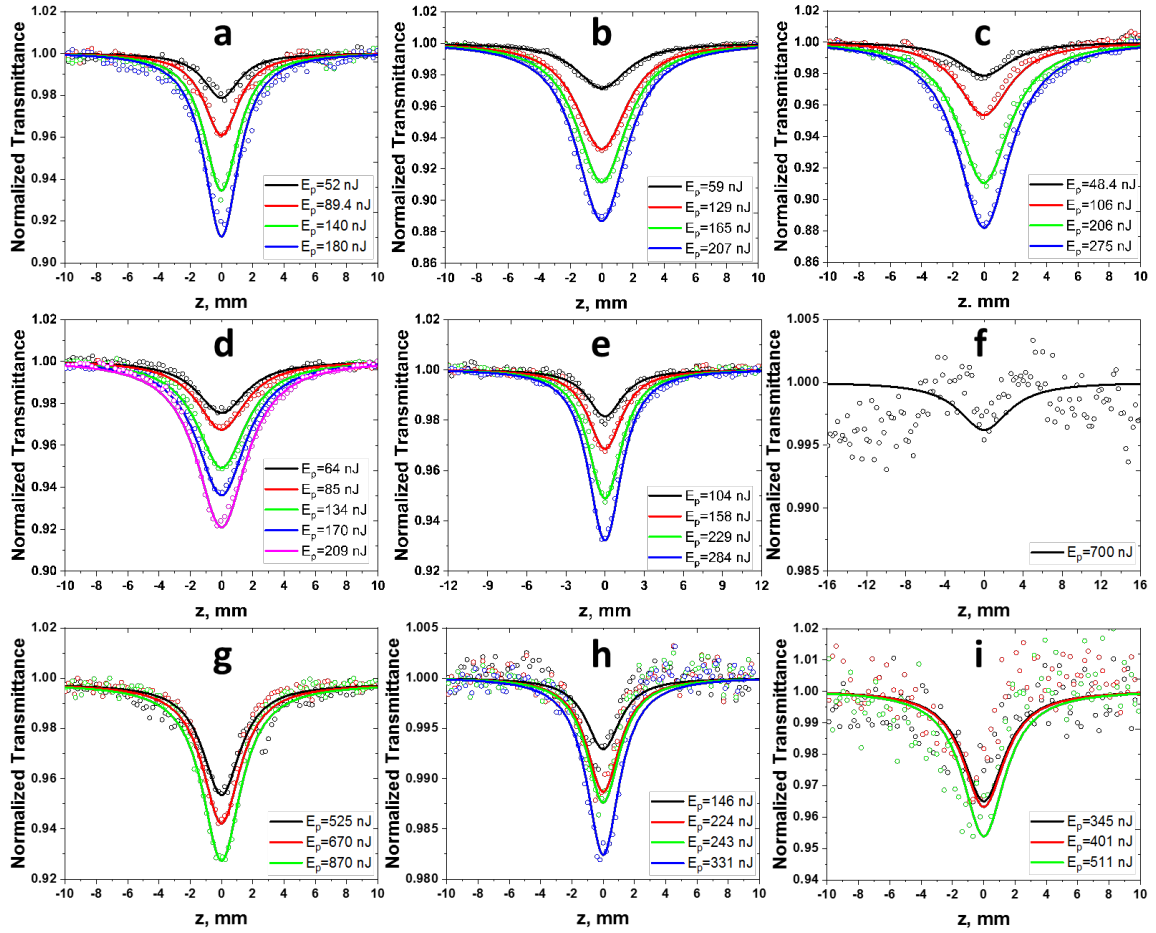


Figure 6. Open aperture Z-scan (circles) and fitting curves (solid lines) for **2** in DCM at (a) 1150 nm, (b) 1200 nm, (c) 1250 nm, (d) 1300 nm, (e) 1350 nm, (f) 1400 nm, (g) 1500 nm, (h) 1550 nm, and (i) 1700 nm.

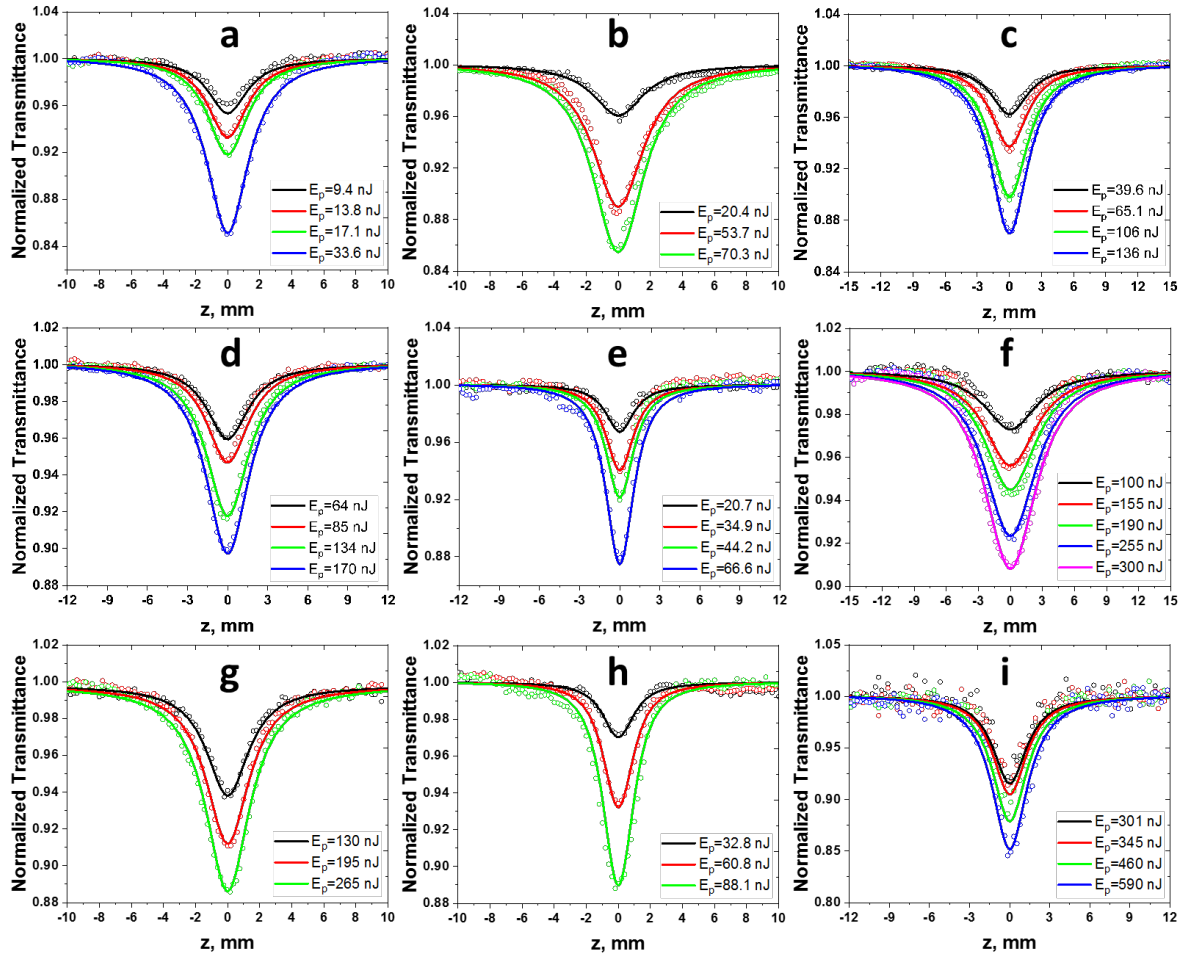


Figure 7. Open aperture Z-scan (circles) and fitting curves (solid lines) for **3** in DCM at (a) 1150 nm, (b) 1200 nm, (c) 1250 nm, (d) 1300 nm, (e) 1350 nm, (f) 1400 nm, (g) 1500 nm, (h) 1550 nm, and (i) 1700 nm.

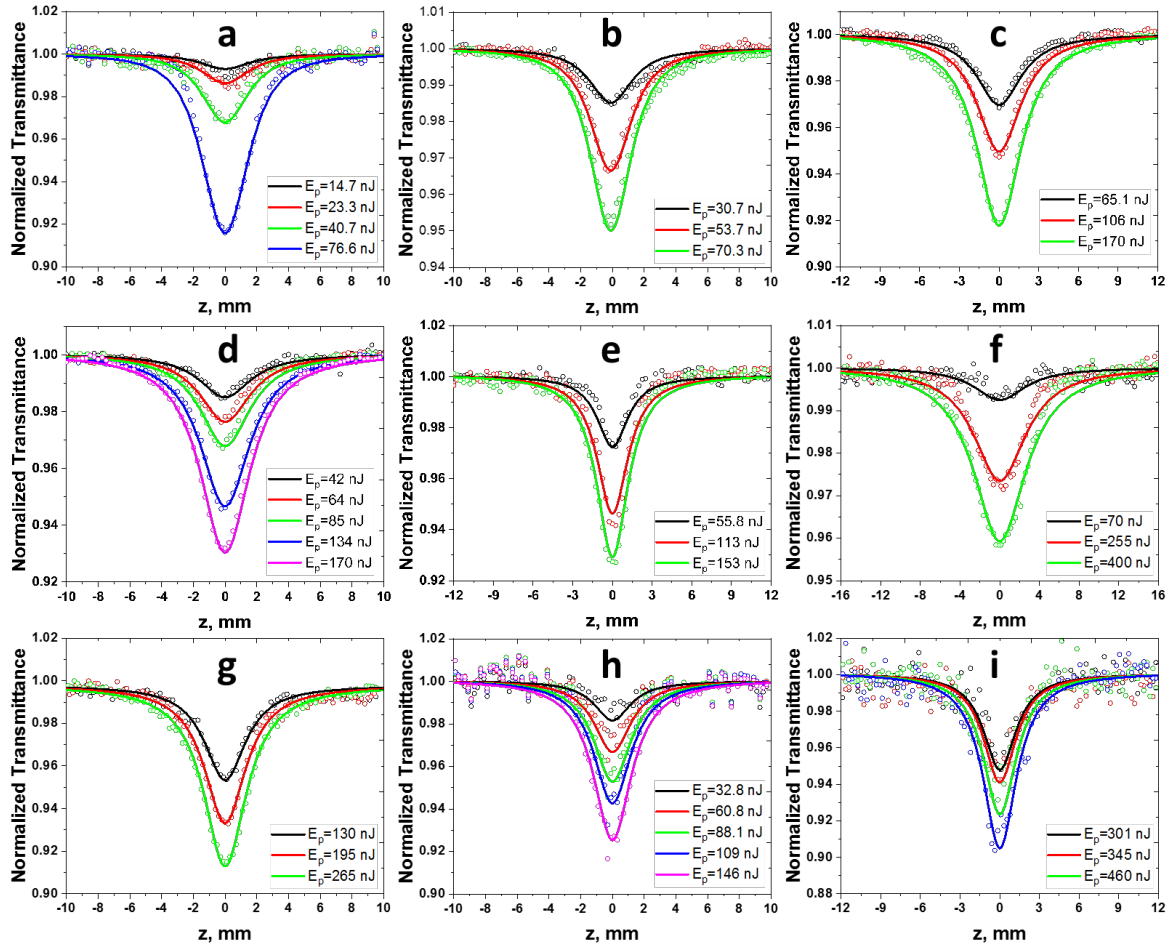


Figure 8. Open aperture Z-scan (circles) and fitting curves (solid lines) for 4 in DCM at (a) 1150 nm, (b) 1200 nm, (c) 1250 nm, (d) 1300 nm, (e) 1350 nm, (f) 1400 nm, (g) 1500 nm, (h) 1550 nm, and (i) 1700 nm.