

## Supporting Information for “Two-photon absorption properties of hexa-substituted benzene derivatives. Comparison between dipolar and octupolar molecules”

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**Synthesis of 6 and 7. A, B, D, and E** were prepared by the literature methods.<sup>1-3</sup> Synthesis of other compounds is described below.

1,3,5-Tribromo-2,4,6-tris(*p*-cyanostyryl)benzene (**C**). Lithium diisopropylamide (LDA) (1.5 M in THF, 13.1 mL, 19.6 mmol) was added dropwise to a stirred solution of **A** (4.3 g, 5.6 mmol) in anhydrous THF (200 mL) at  $-78\text{ }^{\circ}\text{C}$  under nitrogen. This mixture was stirred for 30 min and 4-cyanobenzaldehyde (2.5 g, 19.1 mmol) in THF (50 mL) was slowly added over a period of 10 min. After the mixture was allowed to react for 24 h at room temperature, the reaction was quenched with water and the product was extracted with ethyl acetate. The organic layer was dried with  $\text{MgSO}_4$  and the solvent was removed in vacuo. Recrystallization with acetone gave **C** as a white solid. Yield 2.6 g (67 %); Mp  $> 300\text{ dec.}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 (d, 6H,  $J = 9.0\text{ Hz}$ ), 7.58 (d, 6H,  $J = 9.0\text{ Hz}$ ), 7.02 (d, 3H,  $J = 18.0\text{ Hz}$ ), 6.75 (d, 3H,  $J = 18.0\text{ Hz}$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.6, 139.0, 135.5, 132.8, 131.6, 127.4, 124.2, 119.0, 112.0. Anal. Calcd for  $\text{C}_{33}\text{H}_{18}\text{Br}_3\text{N}_3$ : C, 56.93; H, 2.61; N, 6.04. Found: C, 56.78; H, 2.58; N, 5.99.

1,3,5-Tris(*p*-cyanostyryl)-2,4,6-tris[*p*-(didecylamino)phenylethynyl]benzene (**6**).  $\text{Et}_3\text{N}$  (5.0 mL) was added to a stirred solution of  $\text{Pd}_2\text{Cl}_2(\text{PPh}_3)_2$  (0.010 g, 0.014 mmol), CuI (0.01 g, 0.053 mmol), 4-(didecylamino)phenylacetylene (0.58 g, 1.45 mmol),<sup>4</sup> and **C** (0.20 g, 0.29 mmol) in anhydrous THF/DMF (5/5 mL) under nitrogen. The mixture was stirred at  $100\text{ }^{\circ}\text{C}$  for 36 h. After evaporating solvent and standard work-up procedure, the crude product was purified on a silica gel column using  $\text{CH}_2\text{Cl}_2$ /hexane (1:1) as eluent. Yield 0.25 g (52 %); Mp  $185\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d, 3H,  $J = 18.0\text{ Hz}$ ), 7.79 (d, 3H,  $J = 18.0\text{ Hz}$ ), 7.62 (d, 6H,  $J = 9.0\text{ Hz}$ ), 7.58 (d, 6H,  $J = 9.0\text{ Hz}$ ), 7.16 (d, 6H,  $J = 9.0\text{ Hz}$ ), 6.50 (d, 6H,  $J = 9.0\text{ Hz}$ ), 3.27 (t, 12H,  $J = 6.2\text{ Hz}$ ), 1.59 (t, 12H,  $J = 6.8\text{ Hz}$ ), 1.28 (m, 84H), 0.86 (t, 18H,  $J = 6.0\text{ Hz}$ ).  $^{13}\text{C NMR}$  of this compound cannot be determined due to its low solubility. Anal. Calcd for  $\text{C}_{117}\text{H}_{156}\text{N}_6$ : C, 85.35; H, 9.55; N, 5.10. Found: C, 85.50; H, 9.47; N, 5.05.

1,3,5-Tris(*p*-cyanostyryl)-2,4,6-tris(*p*-dioctylaminostyryl)benzene (**7a**). Synthesized from **E** and *N,N*-dioctylaminobenzaldehyde<sup>5</sup> by the same procedure as described for **C**. Water was added to quench the reaction, and the product was filtered and washed with water followed by recrystallization from chloroform/acetone to give a yellow solid. Mp  $273\text{ }^{\circ}\text{C}$ ; Yield 62 %;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42 (d, 3H,  $J = 16.0\text{ Hz}$ ),  $\delta$  7.37 (d, 6H,  $J = 9.0\text{ Hz}$ ), 7.20 (d, 6H,  $J = 9.0\text{ Hz}$ ), 6.96 (d, 6H,  $J = 9.0\text{ Hz}$ ), 6.93 (d, 3H,  $J = 16.0\text{ Hz}$ ), 6.74 (d, 3H,  $J = 16.0\text{ Hz}$ ), 6.54 (d, 3H,  $J = 16.0\text{ Hz}$ ), 6.38 (d, 6H,  $J = 9.0\text{ Hz}$ ), 3.28 (t, 12H,  $J = 7.2\text{ Hz}$ ), 1.56 (t, 12H,  $J = 7.8\text{ Hz}$ ), 1.29 (m, 60H), 0.86 (t, 18H,  $J = 6.0\text{ Hz}$ ).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.0, 142.3, 136.7, 136.4, 133.1, 132.9, 132.6, 132.3, 127.8, 126.6, 124.2, 123.0, 119.1, 111.8, 110.2, 51.3, 32.3, 30.0, 29.8, 27.8, 27.7, 23.1, 14.6; Anal. Calcd for  $\text{C}_{105}\text{H}_{138}\text{N}_6$ : C, 84.97; H, 9.37; N, 5.66. Found: C, 85.10; H, 9.19; N, 5.61.

1,3,5-tris(*p*-cyanostyryl)-2,4,6-tris[*p*-(bis-*p*-*tert*-butylphenyl)aminostyryl]benzene (**7b**). Synthesized from **E** and 4-[bis-(*p*-*tert*-butylphenyl)amino]benzaldehyde<sup>6</sup> by the same procedure as described for **7a**. Mp  $269\text{ }^{\circ}\text{C}$ ; Yield 65 %;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 (m, 18H),  $\delta$  7.29 (d, 6H,  $J = 9.0\text{ Hz}$ ), 7.26 (d, 3H,  $J = 16.0\text{ Hz}$ ), 7.03 (d, 6H,  $J = 9.0\text{ Hz}$ ), 7.00 (d, 3H,  $J = 16.0\text{ Hz}$ ), 6.99 (m, 12H), 6.75 (d, 3H,  $J$

= 16.0 Hz), 6.75 (d, 6H,  $J = 9.0$  Hz), 6.59 (d, 3H,  $J = 16.0$  Hz), 1.30 (s, 54H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.0, 146.1, 144.1, 141.4, 135.7, 133.3, 132.9, 132.3, 131.7, 129.2, 126.5, 126.1, 126.0, 125.0, 124.3, 121.7, 118.6, 118.4, 110.4, 34.3, 31.4; Anal. Calcd for  $\text{C}_{117}\text{H}_{114}\text{N}_6$ : C, 87.60; H, 7.16; N, 5.24. Found: C, 87.48; H, 7.22; N, 5.31.

**Photophysical studies.** All spectroscopic measurements were performed in toluene (spectroscopic grade). Absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer, and the fluorescence spectra were obtained with a Amico Bowman series 2 luminescence spectrometer. The fluorescence quantum yield was determined by using fluorescein ( $\Phi = 0.95$  in 0.1 M NaOH)<sup>7</sup> or coumarin 307 ( $\Phi = 0.95$  in MeOH)<sup>8</sup> as the reference according to the literature method.<sup>9</sup>

The two-photon absorption cross-sections of **1–7** were determined by two-photon-induced fluorescence method using the femto-second laser pulses as reported.<sup>10</sup> The pulse width and repetition rate of the laser were 160 fs and 90 MHz, respectively. Samples were dissolved in toluene at concentrations of  $5.0 \times 10^{-6}$  M and the two-photon induced fluorescence intensity was measured at 740–940 nm by using fluorescein ( $8.0 \times 10^{-6}$  M, pH = 11) as the reference, whose two-photon properties have been well documented in the literature.<sup>11</sup> The two-photon cross section ( $\delta$ ) was calculated with the equation:  $\delta = [(S_s \Phi_r \phi_r c_r) / (S_r \Phi_s \phi_s c_s)] \delta_r$ , where the subscripts  $s$  and  $r$  refer to the sample and reference molecules. The intensity of the signal collected by a CCD detector was denoted as  $S$ .  $\Phi$  is the fluorescence quantum yield.  $\phi$  is the overall fluorescence collection efficiency of the experimental apparatus. The number density of the molecules in solution was denoted as  $c$ .  $\delta_r$  is the TPA cross section of the reference molecule.

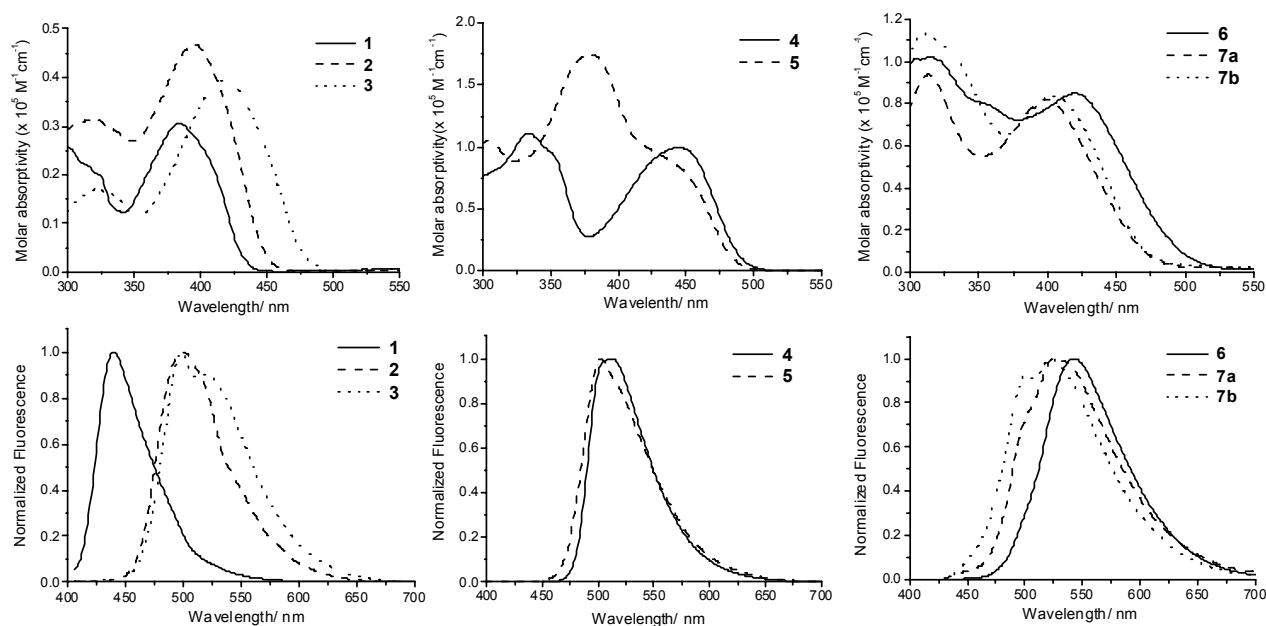


Figure S1. (*upper*) Molar absorptivity and (*below*) normalized emission spectra of **1–7** in toluene.

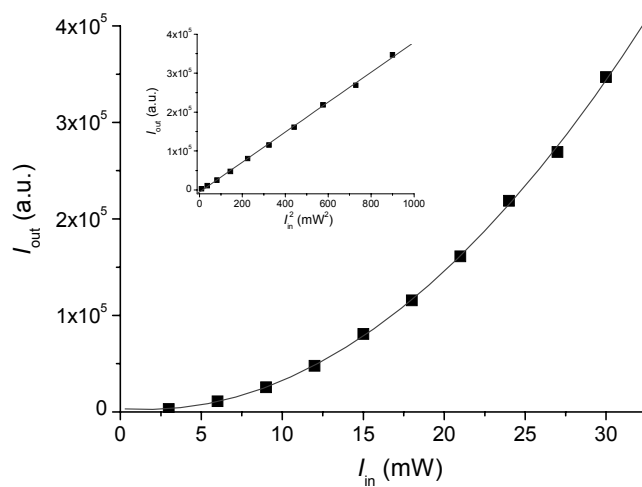
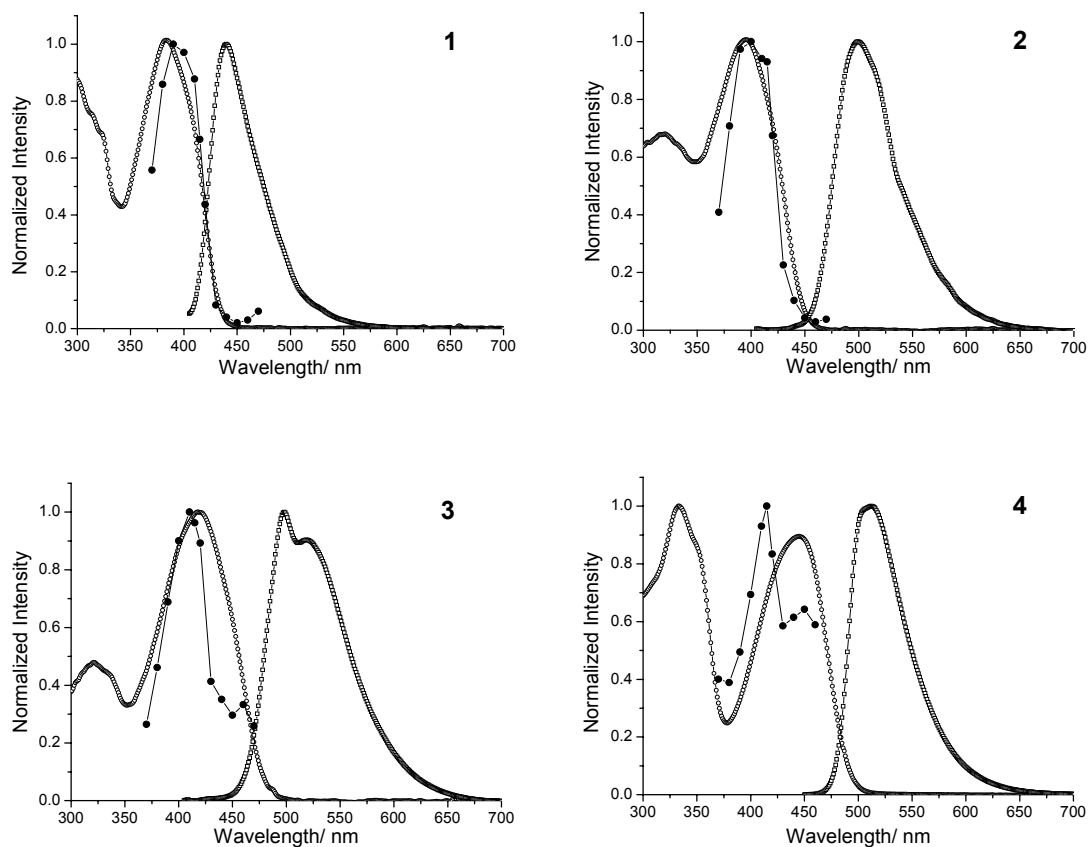


Figure S2. Dependence of output fluorescence intensity ( $I_{out}$ ) of 5  $\mu$ M **6** in toluene on the input laser power ( $I_{in}$ ). The insert shows the linear dependence of  $I_{out}$  on  $I_{in}^2$  (820 nm, 90 MHz,  $\tau = 160$  fs).



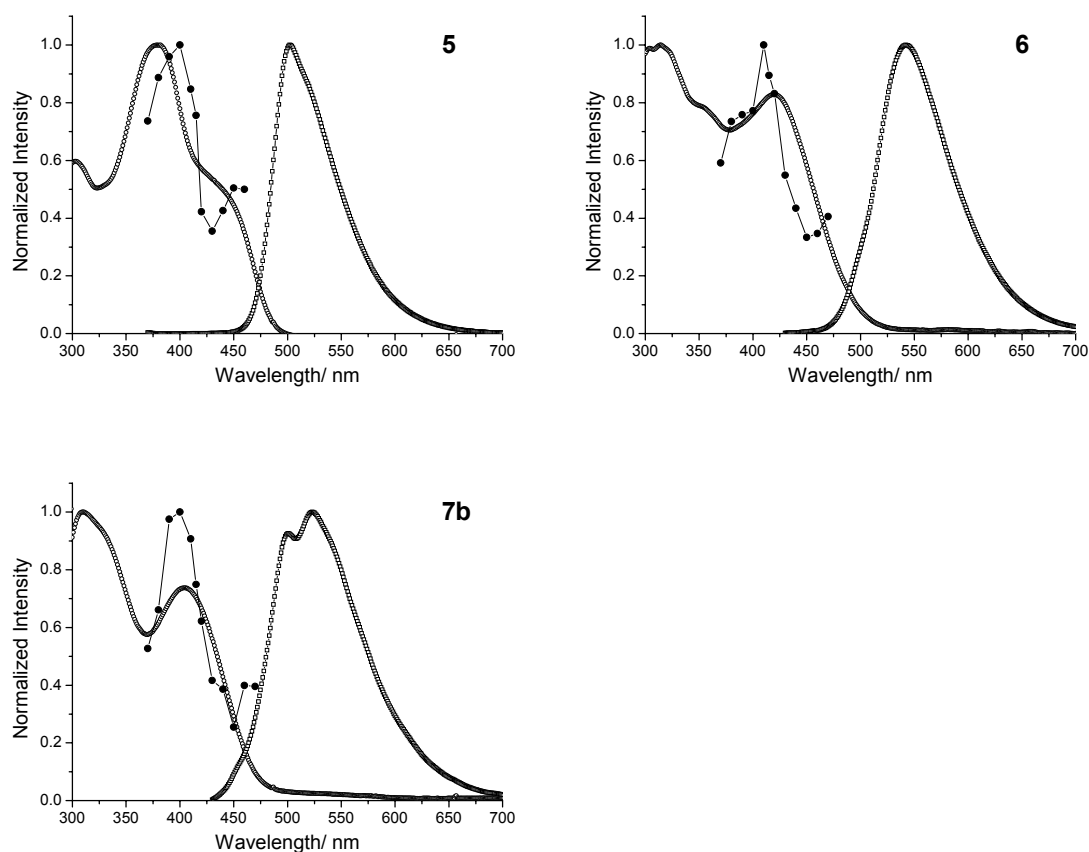


Figure S3. Normalized one-photon absorption ( $\circ$ ), emission ( $\square$ ), and two-photon excitation ( $\bullet$ ) spectra for **1-7** in toluene. The two-photon spectrum is plotted against half the wavelength (twice the photon energy).

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