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.\textsuperscript{1-3} 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 \(-78^\circ\text{C}\) 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 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 dec.; \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.64 (d, 6H, \(J = 9.0\) Hz), 7.58 (d, 6H, \(J = 9.0\) Hz), 7.02 (d, 3H, \(J = 18.0\) Hz), 6.75 (d, 3H, \(J = 18.0\) Hz); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 140.6, 139.0, 135.5, 132.8, 131.6, 127.4, 124.2, 119.0, 112.0. Anal. Calcd for C\(_{33}\)H\(_{18}\)Br\(_3\)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). Et\(_3\)N (5.0 mL) was added to a stirred solution of Pd\(_2\)Cl\(_2\)(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), 4 and C (0.20 g, 0.29 mmol) in anhydrous THF/DMF (5/5 mL) under nitrogen. The mixture was stirred at 100 \(^\circ\text{C}\) for 36 h. After evaporating solvent and standard work-up procedure, the crude product was purified on a silica gel column using CH\(_2\)Cl\(_2\)/hexane (1:1) as eluent. Yield 0.25 g (52%); Mp 185 \(^\circ\text{C}\); \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.88 (d, 3H, \(J = 18.0\) Hz), 7.79 (d, 3H, \(J = 18.0\) Hz), 7.62 (d, 6H, \(J = 9.0\) Hz), 7.58 (d, 6H, \(J = 9.0\) Hz), 7.16 (d, 6H, \(J = 9.0\) Hz), 6.50 (d, 6H, \(J = 9.0\) Hz), 3.27 (t, 12H, \(J = 6.2\) Hz), 1.59 (t, 12H, \(J = 6.8\) Hz), 1.28 (m, 84H), 0.86 (t, 18H, \(J = 6.0\) Hz). \(^{13}\text{C}\) NMR of this compound cannot be determined due to its low solubility. Anal. Calcd for C\(_{117}\)H\(_{156}\)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\textsuperscript{5} 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 \(^\circ\text{C}\); Yield 62%; \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.42 (d, 3H, \(J = 16.0\) Hz), \(\delta\) 7.36 (d, 6H, \(J = 9.0\) Hz), 7.20 (d, 6H, \(J = 9.0\) Hz), 6.93 (d, 3H, \(J = 16.0\) Hz), 6.74 (d, 3H, \(J = 16.0\) Hz), 6.54 (d, 3H, \(J = 16.0\) Hz), 6.38 (d, 6H, \(J = 9.0\) Hz), 3.28 (t, 12H, \(J = 7.2\) Hz), 1.56 (t, 12H, \(J = 7.8\) Hz), 1.29 (m, 60H), 0.86 (t, 18H, \(J = 6.0\) Hz). \(^{13}\text{C}\) NMR of this compound cannot be determined due to its low solubility. Anal. Calcd for C\(_{105}\)H\(_{138}\)N\(_6\): C, 84.97; H, 9.37; N, 5.66. Found: C, 85.10; H, 9.47; N, 5.05.

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\textsuperscript{6} by the same procedure as described for 7a. Mp 269 \(^\circ\text{C}\); Yield 65%; \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.36 (m, 18H), \(\delta\) 7.29 (d, 6H, \(J = 9.0\) Hz), 7.26 (d, 3H, \(J = 16.0\) Hz), 7.03 (d, 6H, \(J = 9.0\) Hz), 7.00 (d, 3H, \(J = 16.0\) Hz), 6.99 (m, 12H), 6.75 (d, 3H, \(J = 9.0\) Hz).
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 an Amico Bowman series 2 luminescence spectrometer. The fluorescence quantum yield was determined by using fluorescein ($\Phi = 0.95$ in 0.1 M NaOH) or coumarin 307 ($\Phi = 0.95$ in MeOH) as the reference according to the literature method.

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. 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. The two-photon cross section ($\delta$) was calculated with the equation: $\delta = [(S_s \Phi_s \phi_s c_s)/(S_r \Phi_r \phi_r c_r)]\delta_r$, 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 ($I_{\text{out}}$) of 5 μM 6 in toluene on the input laser power ($I_{\text{in}}$). The insert shows the linear dependence of $I_{\text{out}}$ on $I_{\text{in}}^2$ (820 nm, 90 MHz, $\tau = 160$ fs).
Figure S3. Normalized one-photon absorption (○), emission (□), and two-photon excitation (●) spectra for 1-7 in toluene. The two-photon spectrum is plotted against half the wavelength (twice the photon energy).

References