

Supporting Information for

Two-photon absorption properties of heterafluorenes and spirobiheterafluorenes bearing aminostyryl arms

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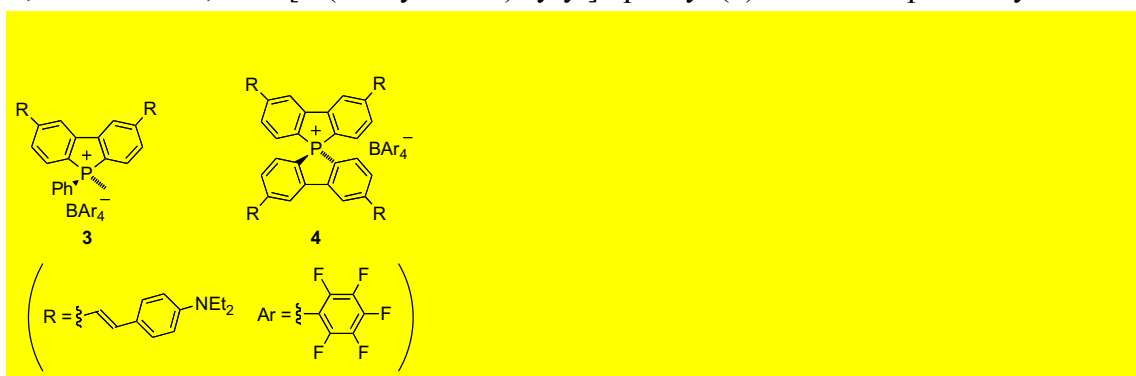
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General. General chemicals were used as received. Spectrochemical grade dichloromethane (Dojindo) was used for optical measurements. All manipulations were performed under argon atmosphere using standard Schlenk technique. Dehydrated solvents (THF and Et₂O) were purchased from Kanto Chemicals and further purified by MBRAUN MB-SPS system equipped with activated alumina and molecular sieve columns before use, and other solvents were purified by using common methods. Column chromatography was carried out with Kanto Silica Gel 60N. Gel permeation liquid chromatography was performed using Japan Analytical Industry LC-918 and LC-908 with JAIGEL 1H+2H columns using chloroform as a solvent. ¹H, ¹³C, ¹¹B, ¹⁹F, ²⁹Si, and ³¹P NMR spectra were recorded on a Bruker DRX-500 spectrometer or a JEOL AL-400 spectrometer. Low resolution mass spectra and high resolution mass spectra were measured with a JEOL JMS-700P (FAB) using *m*-nitrobenzyl alcohol and PEG-600 as matrix and reference, respectively. UV-vis spectra were recorded on a JASCO V-670 spectrophotometer, and fluorescence spectra were measured with a JASCO FP-6500 fluorescence spectrophotometer. All melting points were determined on a Yanaco MP-S3 micro melting point apparatus and uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, the University of Tokyo. The synthesis of 2,2'-dibromo-5,5'-bis[4-(diethylamino)styryl]biphenyl (**5**) has been reported by us.¹



Phosphoniafluorene **3**.

To a THF (20 mL) solution of **5** (0.17 g, 0.26 mmol) was added *n*-BuLi (1.53 M in hexane, 0.34 mL, 0.52 mmol) at -78 °C, and the solution was stirred for 30 min. A THF (10 mL) solution of PhPCl₂ (40 μL, 0.27 mmol) was added to the solution, and the mixture was stirred for 12 h at room temperature. To the mixture was added MeI (5.0 mL, 65 mmol), and the mixture was stirred for 12 h at rt. The reaction was quenched with H₂O. The organic layer was extracted with dichloromethane (20×3 mL), dried over

anhydrous MgSO_4 , and filtered. After the solvent was removed under reduced pressure, the residue containing was dissolved in dichloromethane (20 mL), and $[\text{Li}(\text{OEt}_2)_n][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.30 g, *ca.* 0.3 mmol). The mixture was stirred for 3 d at room temperature, and H_2O was added. The organic layer was extracted with dichloromethane, dried over anhydrous MgSO_4 , and filtered. The removal of the solvent under reduced pressure, followed by vacuum drying gave pure **3** as deep red solids (0.17 g, 57%).

3: deep red solids. mp. 133-134 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.12 (s, 2H), 7.76 (s, 1H), 7.62 (bs, 8H), 7.47 (bs, 4H), 7.36 (d, $J = 14.8$ Hz, 2H), 6.98 (bs, 2H), 6.7 (bs, 4H), 3.42 (bs, 8H), 2.44 (d, $J = 13.5$ Hz, 3H) 1.20 (bs, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 149.1 (bs), 148.5 (s), 147.5 (s), 147.2 (bs), 144.5 (d, $J = 19.6$ Hz), 139.1 (bs), 137.2 (bs), 135.8 (s), 135.0 (s), 131.3 (d, $J = 11.6$ Hz), 130.7 (s), 129.0 (s), 128.1 (d, $J = 12.6$ Hz), 122.9 (s), 120.3 (s), 119.9 (d, $J = 12.6$ Hz), 117.8 (d, $J = 86.6$ Hz), 116.5 (d, $J = 49.1$ Hz), 111.6 (s), 44.6 (s), 12.5 (s), 7.95 (d, $J = 55.3$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 20.8; ^{11}B NMR (128 MHz, CDCl_3) δ -16.9; ^{19}F NMR (376 MHz, CDCl_3) δ -132.35 (bs, 8F), -162.55 (t, $^3J_{\text{FF}} = 14.7$ Hz, 4F), -166.27 (bs, 8F); LRMS (FAB) m/z 622 $[\text{M}-\text{B}(\text{C}_6\text{F}_5)_4]$; LRMS (FAB $^-$) m/z 679 $[\text{B}(\text{C}_6\text{F}_5)_4]^-$. Anal. Calcd. for $\text{C}_{67}\text{H}_{46}\text{BF}_{20}\text{N}_2\text{P}$: C, 61.86; H, 3.56; N, 2.15. Found: C, 62.14; H, 3.75; N, 1.88.

Spirobiphosphoniafluorene **4**.

To an Et_2O (20 mL) suspension of **5** (0.17 g, 0.26 mmol) was added *n*-BuLi (1.53 M in hexane, 0.34 mL, 0.52 mmol) at room temperature, and the mixture was stirred for 20 min. An Et_2O (10 mL) solution of $\text{P}(\text{O})(\text{OPh})_3$ (45 mg, 0.14 mmol) was added to the solution, and the reaction mixture was stirred for further 12 h. To the mixture was added an aq. HCl (1 M, 6 mL) solution of $[\text{Li}(\text{OEt}_2)_n][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.54 g, *ca.* 0.5 mmol), and the stirring was continued for 1 h. The reaction was quenched by H_2O . The organic layer was extracted with dichloromethane (20 \times 3 mL), dried over anhydrous MgSO_4 , and filtered. After removal of the solvent under reduced pressure, the crude material was separated by GLPC. The solvent was removed, and the residue was dried *in vacuo* to give **4** as deep red solids (70 mg, 32%).

4: deep red solids. mp. 168-169 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.30 (s, 4H), 7.43-7.51 (m, 20 H), 7.03 (d, $J = 16.1$ Hz, 4H), 6.72 (d, $J = 8.7$ Hz, 8 H), 3.43 (q, $J = 7.0$ Hz, 16H), 1.21 (t, $J = 7.1$ Hz, 24H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 149.0 (bs),

148.7 (s), 147.6 (s), 147.1 (bs), 146.2 (d, $J = 21.2$ Hz), 137.2 (bs), 134.8 (s), 131.7 (d, $J = 12$ Hz), 128.9(s), 128.1 (d, $J = 13.2$ Hz), 122.6 (s), 120.2 (s), 119.8 (d, $J = 10.7$ Hz), 114.0 (s), 113.2 (s), 111.4 (s), 44.4 (s), 12.3 (s); ^{31}P NMR (162 MHz, CDCl_3) δ 19.0; ^{11}B NMR (128 MHz, CDCl_3) δ -16.6; ^{19}F NMR (376 MHz, CDCl_3) δ -132.34(bris, 8F), -162.77 (t, $^3J_{\text{FF}} = 14.7$ Hz, 4F), -166.38 (bris, 8F); LRMS (FAB) m/z 1028 [M-B(C₆F₅)₄]; LRMS (FAB⁻) m/z 679 [B(C₆F₅)₄]⁻. Anal. Calcd. for C₉₆H₇₆BF₂₀N₄P: C, 67.53; H, 4.49; N, 3.28. Found: C, 67.40; H, 4.76; N, 3.21.

3: λ_{max} 464 nm, ϵ 57000

4: λ_{max} 496 nm, ϵ 103000

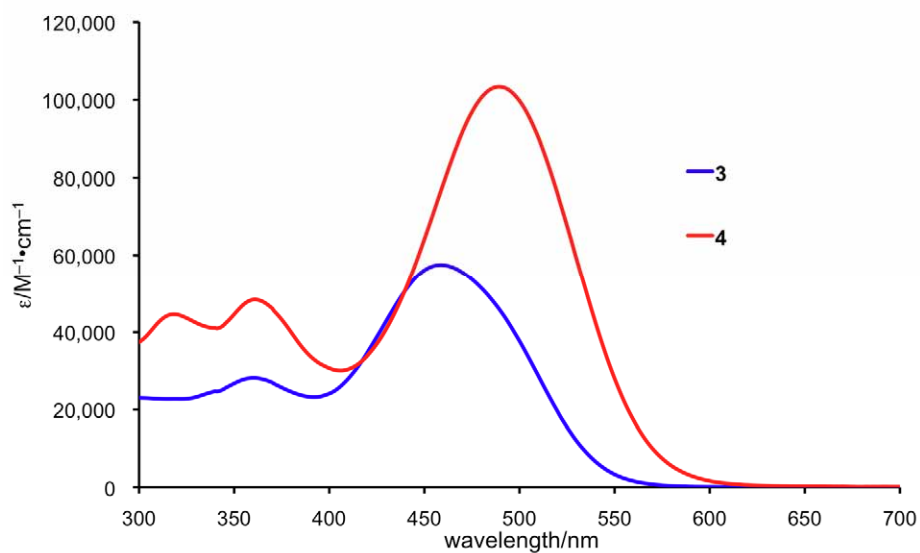


Fig. S1. UV-vis spectra of **3** and **4** in dichloromethane.

3: λ_{em} 647 nm, Φ 0.52

4: λ_{em} 715 nm, Φ 0.04

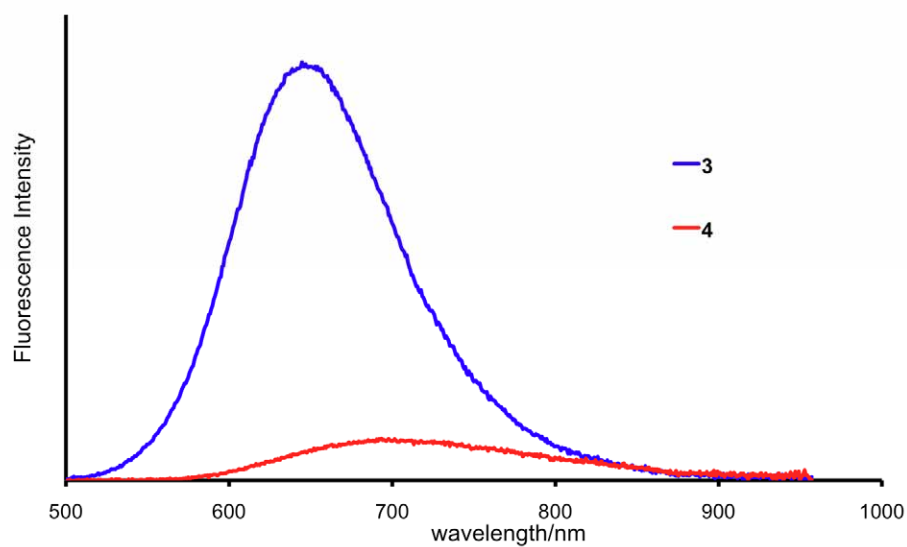


Fig. S2. Fluorescence spectra of **3** and **4** in dichloromethane.

3: λ_{max} 460 nm, ϵ 42000

4: λ_{max} 495 nm, ϵ 82000

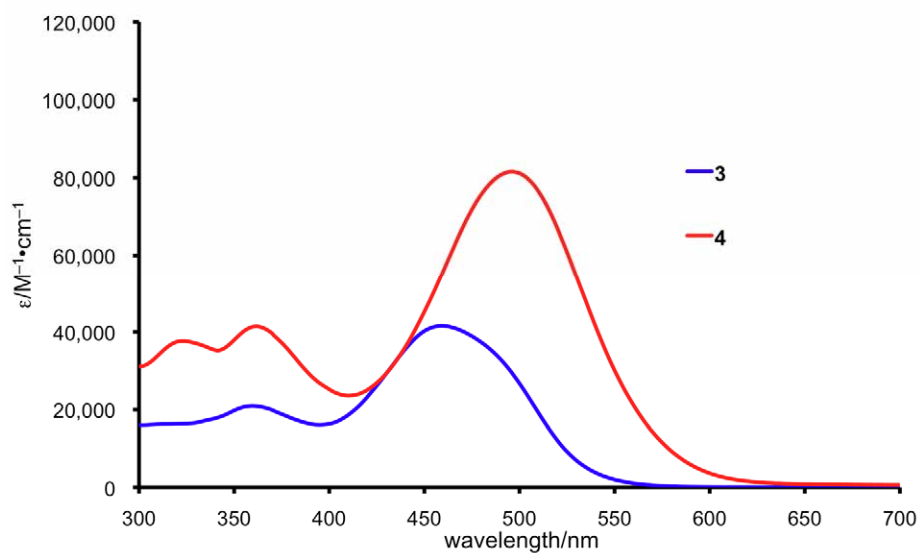


Fig. S3. UV-vis spectra of **3** and **4** in toluene.

3: λ_{em} 648 nm, Φ 0.62

4: λ_{em} 695 nm, Φ 0.10

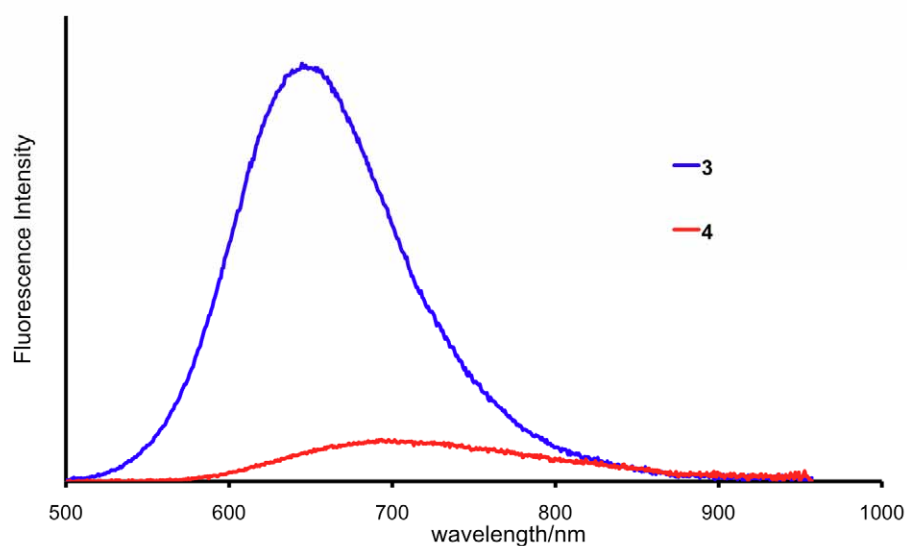


Fig. S4. Fluorescence spectra of **3** and **4** in toluene.

3: λ_{max} 430 nm, ϵ 52000

4: λ_{max} 467 nm, ϵ 89000

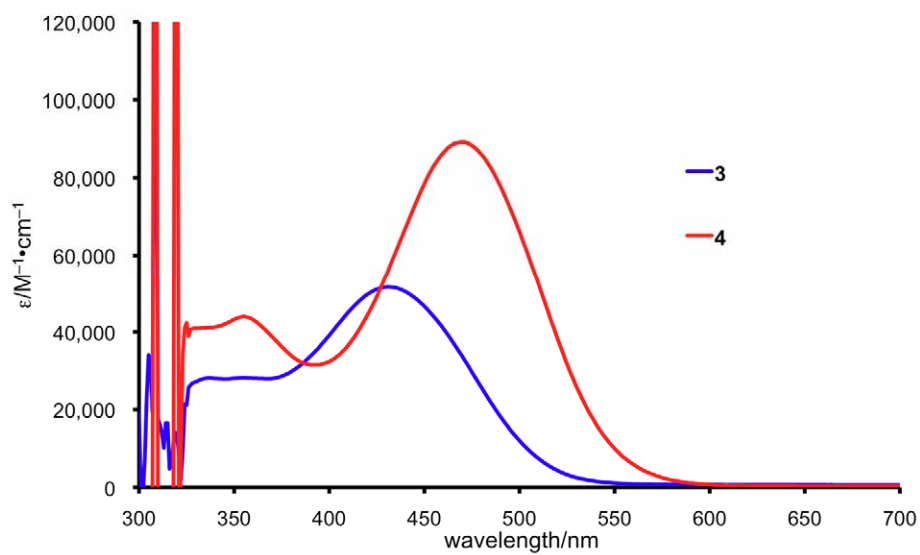


Fig. S5. UV-vis spectra of **3** and **4** in acetone.

Two-photon absorption measurement and analysis

Two-photon absorption (TPA) spectra of the compounds were measured by the open-aperture Z-scan method² by changing the incident wavelength. The optical setup for the Z-scan measurement was reported previously³. As a light source, femtosecond optical parametric amplifier (*SpectraPhysics OPA-800*) operating at 1 kHz pumped by a Ti:sapphire regenerative amplifier system (*SpectraPhysics Spitfire, Merlin, Tsunami, and Millennia*) was used for the measurement. The pulse width of the laser beam (typically 140 fs) was measured for each set of measurements and used for the calculation of the TPA coefficients. We put a small aperture away from the focusing lens to form an Airy-like spatial profile, which is close to a Gaussian distribution. Therefore, the incident pulses can be regarded as temporally and spatially Gaussian. We measured at least four scans with different optical powers (0.05–0.5 mW at the sample position) for each sample at a wavelength in order to check the power-dependence of the recorded nonlinear absorption signal, i.e. a dip of the open-aperture trace. The Rayleigh range of the setup varies depending on the incident wavelength, but was typically 4–5 mm, which is sufficiently longer than the optical path length (1 mm) of the sample solution hold in a quartz cuvette, filling the optically thin condition. Typical open-aperture traces observed for the compounds shown in Fig. S6.

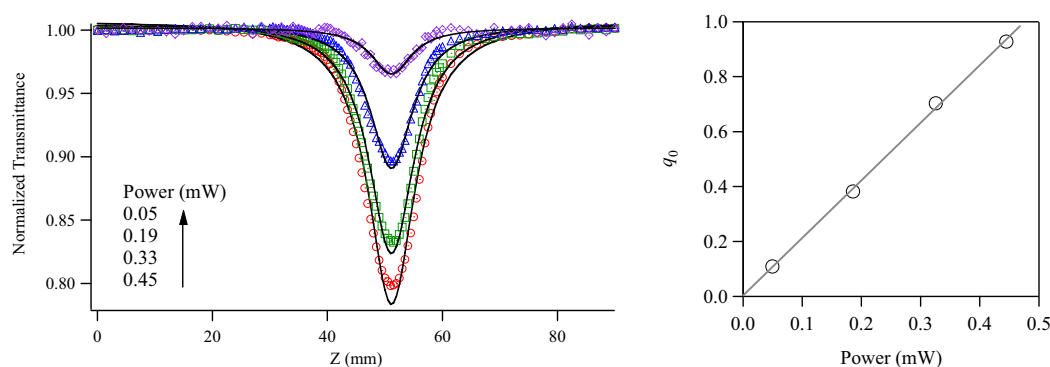


Fig. S6. Left panel: the recorded open-aperture traces for Compound **2** at 874 nm (markers) with fitting curves based on Eqs. 1 and 2 (solid lines). Right panel: the plot of the obtained two-photon absorbance q_0 from the curve-fits against the incident power (right).

The recorded traces are analyzed with curve-fit with the theoretical formula for the energy transmittance of temporally- and spatially-Gaussian pulses through a TPA media

as:⁶

$$T(\zeta) = T_l \frac{1}{\sqrt{\pi q(\zeta)}} \int_{-\infty}^{\infty} \ln[1 + q(\zeta)e^{-x^2}] dx$$

(1)

with

$$q(\zeta) = \frac{q_0}{1 + \zeta^2},$$

(2)

where ζ is the normalized sample position defined as $\zeta = (z - z_0)/z_R$ (z_0 and z_R are the focal position and the Rayleigh range, respectively). $T_l = (1 - R)^2 e^{-\alpha^{(1)}L}$ means the transmittance by the one-photon absorption, where $\alpha^{(1)}$ is the one-photon (or linear) absorption coefficient, L is the physical length of the sample, and R is the Fresnel reflectance at the cell surface. q_0 is the two-photon absorbance at the focal position ($\zeta = 0$) defined as,

$$q_0 = \alpha^{(2)} I_0 (1 - R) L_{eff}, \quad (3)$$

where $\alpha^{(2)}$ is TPA coefficient, I_0 is the on-axis peak intensity of the incident pulse, and L_{eff} is the effective path length defined as $L_{eff} = [1 - \exp(-\alpha^{(1)}L)] / \alpha^{(1)}$.

The q_0 's obtained by curve fitting with Eqs. 1 and 2 to the open-aperture traces are plotted against the incident power (the left panel of Fig. S6), exhibiting a good proportionality relation. As the incident power is proportional to I_0 , the observed nonlinear absorption can be assigned to simultaneous TPA. From slope of the plot, $\alpha^{(2)}$ was determined and then TPA cross section $\sigma^{(2)}$ was obtained by using the convention $\sigma^{(2)} = \hbar\omega \alpha^{(2)} / N$, where N is the number density of molecules and $\hbar\omega$ is the photon energy of the incident light. In addition to the compounds, our in-house reference material, MPPBT^{4,5,6} dissolved in dimethylsulfoxide, was also measured at the same time for each measurements. The obtained $\sigma^{(2)}$ spectra of the samples were corrected based on that of MPPBT.

References

- 1) T. Agou, Md. D. Hossain and T. Kawashima, *Chem. Eur. J.*, in press.
- 2) M. Sheik-Bahae, A. A. Said, T. H. Wei, D. G. Hagen and E. W. Van Stryland, *IEEE J. Quant. Electr.*, 1990, **26**, 760-769.
- 3) K. Kamada, K. Matsunaga, A. Yoshino and K. Ohta, *J. Opt. Soc. Am. B*, 2003, **20**, 529-537.
- 4) K. Kamada, K. Ohta, Y. Iwase and K. Kondo, *Chem. Phys. Lett.*, 2003, **372**, 386-393.
- 5) K. Kamada and K. Ohta, *Proceedings of SPIE*, 2007, **6470**, 6470S1-6470S8.
- 6) R. L. Sutherland, *Handbook of Nonlinear Optics*, 2nd Ed., Marcel Dekker, New York, **2003**, Chap. 7, p. 463.