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Two-photon Absorption Properties of 9,10-Disubstituted 2,6-Bis(*p*-dihexylaminostyryl)Anthracene Derivatives. Effect of 9,10-Substituents

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Abstract A series of 2,6-bis(*p*-dihexylaminostyryl)anthracene derivatives having phenyl, styryl, and phenylethynyl groups at 9,10-positions (**1–4**) have been synthesized and their two-photon cross-sections were determined. Overall, the wavelengths of the longest wavelength absorption band and emission spectra increase with increase in the conjugation length and the electron withdrawing ability of the 9,10-substituents. All compounds show two-photon cross sections in the range of 740−3940 GM at 780−960 nm, which increase significantly by the donor and acceptor groups at 9,10-positions. In addition, Ph and phenylethynyl groups are better when compared to the styryl group at the 9,10-positions in terms of the two-photon action cross section. From a practical perspective, **1a, 2a–c,** and **4b** showed significant two-photon action cross-section and are most useful for applications that use two-photon excited fluorescence.

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Introduction

Recent years witnessed growing interest to develop efficient organic two photon materials for possible applications in two-photon fluorescence imaging [1, 2], optical power limiting [3, 4], two-photon upconversion lasing [4, 5], 3D optical data storage [6], 3D microfabrication [6, 7], and photodynamic therapy [8]. A variety of donor–bridge–acceptor (D–π–A) dipoles, donor–bridge–donor (D–π–D) quadruples, and octupoles were developed and their structure–property relationship had been investigated [9–28]. The results of these studies reveal that the TPA cross section increases with the donor–acceptor strength, conjugation length, and the planarity of the π-center.

Recently, we have reported that 2,6-bis(*p*-dialkylaminostyryl)anthracene derivatives (**1a,c** and **2a,c**) exhibited large two photon cross sections (δ_{TPA}) in the range of 700–2,500 GM [24, 26]. The δ_{TPA} value of 9,10-CN derivative (**1c**) was 2-fold larger than that of **1a** but the two-photon action cross section ($\Phi\delta_{TPA}$) was decreased due to poor fluorescence quantum yield. Optimization of $\Phi\delta_{TPA}$ was established with *p*-cyanophenyl groups at the 9,10-positions (**2c**). When the conjugation length was increased as 2,6-bis[4-(*p*-dialkylaminostyryl)styryl]anthracene, the δ_{TPA} value remained nearly the same as that of **1a**, but increased to 2,580 and 5,530 GM, when OMe and CN groups were introduced at 9,10-positions, respectively [28]. On the other hand, the δ_{TPA} values of 9,10-bis(arylethynyl)anthracene derivatives were smaller than that of **1a**, and the δ_{TPA}/MW value decreased with the conjugations length [25]. Therefore, it was difficult to make a proper conclusion on the effects of the 9,10-subsitutents on the δ_{TPA} values.

In order to provide a better insight into the effects of 9,10-subsitutents, we have synthesized a series of 2,6-bis(*p*-dihexylaminostyryl)anthracene derivatives having phe-

nyl, styryl, and arylethynyl groups at the 9,10-positions (**2b, 3a–c, 4a–c**) and investigated their one- and two-photon absorption properties. The chromophores examined are shown in Scheme 1. By comparing with the existing data for **1a,c** and **2a,c** [26], the effects of 9,10-substituents on the δ_{TPA} values of the anthracene derivatives is assessed.

Experimental section

Synthesis

2,6-Bis(diethylphosphorylmethyl)-9,10-dibromoanthracene A mixture of 2,6-dimethyl-9,10-dibromoanthracene (2.6 g, 7.3 mmol), NBS (2.9 g, 16 mmol), and benzoyl peroxide (71 mg, 0.29 mmol) in benzene (100 ml) was refluxed for 4 h. The mixture was poured into methanol, and the precipitate that collected was dried by vacuum. This intermediate was added to triethyl phosphate (50 ml), and the resulting solution was refluxed for 12 h. The solvent was removed by in vacuo and the residue was purified by column chromatography on silica gel using ethyl acetate/ CH_2Cl_2 (2:1) as the eluent. Yield: 3.6 g (76%); mp 251–253 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (d, J=9.0 Hz, 2H), 8.45 (d, J=3.0 Hz, 2H), 7.60 (dd, J=9.0 Hz, 3.0 Hz, 2H), 4.07 (m, 8H), 3.42 (d, J=21 Hz, 4H), 1.27 ppm (t, J=7.5 Hz, 12H).

2,6-Bis[(p-dihexylamino)styryl]-9,10-dibromoanthracene (A) LDA (1.5 M in cyclohexane) (3.4 ml, 5.1 mmol) was added dropwise to a stirred solution of 2,6-bis(diethylphos-phorylmethyl)-9,10-dibromoanthracene (2.67 g, 2.1 mmol) in anhydrous THF (100 ml) at −78 °C under argon. The mixture was stirred for 1 h and then *p*-dihexylaminobenzal-dehyde (1.5 g, 5.2 mmol) in THF (20 ml) was added dropwise over a period of 3 min. After the mixture was stirred for 2 h at −78 °C and for 6 h at room temperature, 1 ml of water was added and the solvent was evaporated. The residue was dissolved into CH_2Cl_2 and washed several times with water. The solvent was evaporated and the crude product was separated by column chromatography on silica gel using hexane/CH_2Cl_2 (3:1) as the eluent. Yield: 1.98 g (52%); mp 171–173 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.46 (d, J=9.0 Hz, 2H), 8.36 (d, J=3.0 Hz, 2H), 7.86 (dd, J=9.0 Hz, 3.0 Hz, 2H), 7.46 (d, J=9.0 Hz. 4H), 7.25 (d, J=15.0 Hz, 2H), 7.14 (d, J=15.0 Hz, 2H), 6.65 (d, J=9.0 Hz, 4H), 3.30 (t, J=7.5 Hz, 8H), 1.65 (m, 8H), 1.34 (m, 24H), 0.92 ppm (t, J=6.0 Hz, 12H). Elemental analysis: calcd (%) for $C_{54}H_{70}Br_2N_2$: C, 71.51; H, 7.78; N, 3.09. Found: C, 71.58; H, 7.81; N, 3.12.

2,6-Bis[(p-dihexylamino)styryl]-9,10-bis(p-N,N-didecylami-nophenyl)anthracene (2b) A solution of *p*-didecylamino-phenylboronoic acid (0.37 g, 0.73 mmol), A (0.20 g, 0.22 mmol), Pd(PPh$_3$)$_4$ (0.055 g, 0.0.31 mmol) and toluene (7 ml) was degassed and then Na$_2$CO$_{3(aq)}$ (2.0 M, 4.0 ml) was added. The suspension was refluxed overnight under nitrogen. The mixture was extracted with CH_2Cl_2 and solvent was removed in vacuo. The solvent was evaporated and the crude product was separated by column chroma-tography on silica gel using hexane/CH_2Cl_2 (4:1) as the eluent. Yield: 0.23 g (71%); mp 79–81 °C; ^{1}H NMR

Scheme 1 Structure of the two-photon dyes considered in this paper

X = H (**a**), (C$_{10}$H$_{21}$)$_2$N (**b**), CN (**c**)
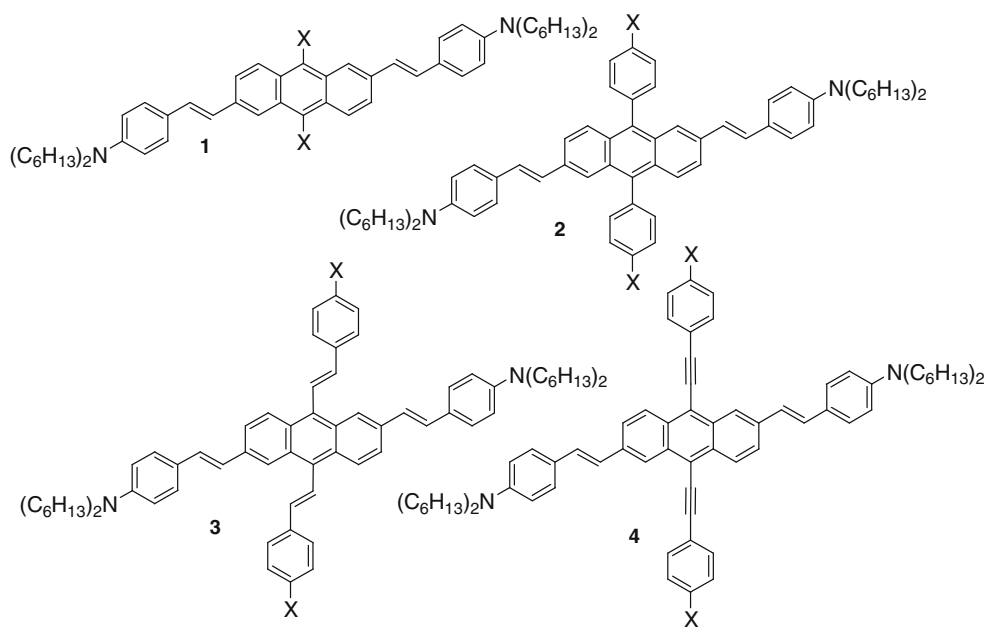
(300 MHz, CDCl$_3$): δ 7.84 (d, J=9.0 Hz, 2H), 7.75 (d, J=3.0 Hz, 2H), 7.65 (dd, J=9.0 Hz, 3.0 Hz, 2H) 7.41 (d, J=9.0 Hz, 4H), 7.36 (d, J=9.0 Hz, 4H), 7.08 (d, J=15.0 Hz, 2H), 7.01 (d, J=15.0 Hz, 2H), 6.91 (d, J=9.0 Hz, 4H), 6.64 (d, J=9.0 Hz, 4H), 3.45 (t, J=7.5 Hz, 8H), 3.30 (t, J=7.5 Hz, 8H), 1.79 (m, 8H), 1.62 (m, 8H), 1.35–1.46 (m, 80H), 0.93 ppm (m, 24H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 147.9, 147.7, 137.1, 134.4, 132.7, 131.1, 130.5, 128.7, 128.0, 126.0, 125.7, 125.1, 124.9, 121.9, 111.9, 111.6, 100.3, 51.7, 51.5, 51.3, 32.2, 32.0, 30.1, 29.9, 29.7, 27.8, 27.6, 27.5, 27.1, 23.0, 22.9, 14.4, 14.3 ppm. Elemental analysis: Calcd (%) for C$_{106}$H$_{162}$N$_4$: C, 85.31; H, 10.94; N, 3.75. Found: C, 85.40; H, 10.89; N, 3.70.

2,6-Bis(p-N,N-dihexylaminostyryl)-9,10-bis(styryl)anthracene (3a) A pressure tube containing a mixture of styrene (0.51 g, 4.7 mmol), **A** (0.20 g, 0.22 mmol), Pd(OAc)$_2$ (4.9 mg, 0.022 mmol), tris-(o-tolyl)phosphine (0.045 g, 0.15 mmol), Et$_3$N (1 ml) and MeCN (1 ml) were mixed in sealed tube and refluxed for 24 h. The mixture was extracted with CH$_2$Cl$_2$ and the solvent was removed in vacuo. The crude product was separated by column chromatography on silica gel using hexane/CH$_2$Cl$_2$ (4:1) as the eluent. Yield: 0.14 g (65%); mp 122–124 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.28 (d, J=9.0 Hz, 2H), 8.14 (d, J=3.0 Hz, 2H), 7.86 (d, J=15.0 Hz, 2H), 7.73 (dd, J=9.0 Hz, 3.0 Hz, 2H), 7.71 (d, J=7.5 Hz, 4H), 7.48 (m, 4H), 7.40 (m, 6H), 7.13 (d, J=15.0 Hz, 2H), 7.06 (d, J=15.0 Hz, 2H), 6.94 (d, J=15.0 Hz, 2H), 6.60 (d, J=9.0 Hz, 4H), 3.27 (t, J=7.5 Hz, 8H), 1.58 (m, 8H), 1.31 (m, 24H), 0.90 ppm (t, J=7.5 Hz, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.0, 137.7, 137.4, 135.1, 134.7, 132.3, 130.2, 130.0, 129.4, 129.4, 129.1, 128.1, 126.9, 125.6, 124.7, 124.6, 124.3, 122.7, 111.8, 51.3, 32.0, 27.5, 27.1, 22.9, 14.3 ppm. Elemental analysis: Calcd (%) for C$_{70}$H$_{84}$N$_2$: C, 88.18; H, 8.88; N, 2.94. Found: C, 88.26; H, 8.81; N, 3.01.

2,6-Bis(p-N,N-dihexylaminostyryl)-9,10-bis(p-N,N-didecylaminostyryl)anthracene (3b) Synthesized by the same procedure as described for **3a** except that *p*-dihexylaminostyrene was used instead of styrene. The crude product was separated by column chromatography on silica gel using hexane/CH$_2$Cl$_2$ (3:1) as the eluent. Yield: 0.17 g (59%); mp 97–99 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.36 (d, J=9.0 Hz, 2H), 8.22 (d, J=3.0 Hz, 2H), 7.72 (dd, J=9.0 Hz, 3.0 Hz, 2H), 7.66 (d, J=15.0 Hz, 2H), 7.60 (d, J=9.0 Hz, 4H), 7.42 (d, J=9.0 Hz, 4H), 7.14 (d, J=15.0 Hz, 2H), 7.08 (d, J=15.0 Hz, 2H), 6.84 (d, J=15.0 Hz, 2H), 6.74 (d, J=9.0 Hz, 4H), 6.62 (d, J=9.0 Hz, 4H), 3.36 (t, J=7.5 Hz, 8H), 3.28 (t, J=7.5 Hz, 8H), 1.64 (m, 16H), 1.30–1.37 (m, 80H), 0.92 ppm (m, 24H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.2, 147.9, 137.4, 134.7, 132.8, 130.4, 129.6, 128.9, 128.1, 128.0, 127.3, 125.2, 125.0, 124.7, 122.2, 120.3, 120.3, 111.9, 111.9,

51.4, 51.3, 32.0, 31.9, 27.6, 27.5, 27.2, 27.1, 24.8, 24.5, 23.2, 23.0, 22.7, 22.9, 14.4, 14.3 ppm. Elemental analysis: Calcd (%) for C$_{110}$H$_{166}$N$_4$: C, 85.54; H, 10.83; N, 3.63. Found: C, 85.48; H, 10.86; N, 3.67.

2,6-Bis(p-N,N-dihexylaminostyryl)-9,10-bis(p-cyanostyryl)anthracene (3c) Synthesized by the same procedure as described for **3a** except that styrene was replaced with *p*-cyanostyrene. The crude product was separated by column chromatography on silica gel using hexane/CH$_2$Cl$_2$ (2:1) as the eluent. Yield: 0.11 g (51%); Mp 110–112 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.10 (d, J=9.0 Hz, 2H), 7.95 (d, J=3.0 Hz, 2H), 7.80 (d, J=15.0 Hz, 2H), 7.74 (dd, J=9.0 Hz, 3.0 Hz, 2H), 7.70 (d, J=9.0 Hz, 4H), 7.66 (d, J=9.0 Hz, 4H), 7.44 (d, J=9.0 Hz, 4H), 7.16 (d, J=15.0 Hz, 2H), 7.04 (d, J=15.0 Hz, 2H), 6.86 (d, J=15.0 Hz, 2H), 6.64 (d, J=9.0 Hz, 4H), 3.31 (t, J=7.5 Hz, 8H), 1.62 (m, 8H), 1.34 (m, 24H), 0.92 ppm (t, J=7.5 Hz, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.4, 137.0, 132.0, 131.9, 131.7, 130.6, 128.4, 127.9, 126.6, 124.7, 124.2, 124.0, 123.2, 118.7, 117.0, 116.0, 111.7, 111.5, 100.7, 96.4, 51.4, 32.1, 27.5, 27.1, 23.0, 14.3 ppm. Elemental analysis: Calcd (%) for C$_{72}$H$_{82}$N$_4$: C, 86.18; H, 8.24; N, 5.58. Found: C, 86.26; H, 8.21; N, 5.65.

2,6-Bis(p-N,N-dihexylaminostyryl)-9,10-bis(phenylethynyl)anthracene (4a) A solution of phenylacetylene (0.26 g, 2.0 mmol) in toluene (3 ml) was added to a degassed mixture containing **A** (0.20 g, 0.32 mmol), Pd(PPh$_3$)$_4$ (0.05 g, 0.041 mmol), CuI (8.0 mg, 0.041 mmol), and (i-Pr)$_2$NH (7 ml) in toluene (20 ml) was added by a syringe. The suspension was stirred overnight at 80 °C. The solvent was removed in vacuo and the product was separated by column chromatography on silica gel using ethyl acetate/hexane (2:1) as the eluent. Yield: 77 mg (37%). Mp 168–1170 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (d, J=9.0 Hz, 2H), 8.43 (d, J=3.0 Hz, 2H), 7.82 (m, 6H), 7.49 (m, 10H), 7.26 (d, J=15.0 Hz, 2H), 7.15 (d, J=15.0 Hz, 2H), 6.68 (d, J=9.0 Hz, 4H), 3.32 (t, J=7.5 Hz, 8H), 1.64 (m, 8H), 1.36 (m, 24H), 0.93 ppm (t, J=7.5 Hz, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.2, 136.5, 132.4, 132.0, 131.9, 130.2, 128.8, 128.7, 128.4, 127.5, 124.9, 124.7, 124.5, 124.1, 124.0, 117.7, 111.8, 102.2, 87.2, 51.3, 32.0, 30.0, 27.1, 23.0, 14.4 ppm. Elemental analysis: Calcd (%) for C$_{106}$H$_{162}$N$_4$: C, 88.56; H, 8.49; N, 2.95. Found: C, 88.49; H, 8.54; N, 3.01.

2,6-Bis(p-N,N-dihexylaminostyryl)-9,10-bis[(p-N,N-didecylamino)phenylethynyl]anthracene (4b) Synthesized by the same procedure as described for **4a** except that 4-(N,N-didecylamino)phenylacetylene was used instead of phenyacetylene. The crude product was separated by column chromatography on silica gel using hexane/CH$_2$Cl$_2$ (3:1) as the eluent. Yield: 0.15 g (43%); mp 123–125 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.60 (d, J=9.0 Hz, 2H), 8.52 (d, J=

3.0 Hz, 2H), 7.86 (dd, J=9.0 Hz, 3.0 Hz, 2H), 6.65 (d, J= 6.0 Hz, 40H), 7.50 (d, J=9.0 Hz, 4H), 7.28 (d, J=16.5 Hz, 2H), 7.16 (d, J=16.5 Hz, 2H), 6.71 (d, J=9.0 Hz, 4H), 6.66 (d, J=9.0 Hz, 4H), 3.32 (m, 16H), 1.63 (m, 16H), 1.32 (m, 80H), 0.91 ppm (m, 24H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.3, 148.1, 136.1, 133.3, 132.3, 131.8, 129.8, 128.2, 127.8, 125.4, 124.9, 124.4, 124.0, 118.0, 111.9, 111.6, 109.5, 103.9, 85.2, 51.4, 51.3, 32.2, 29.9, 29.8, 29.8, 29.6, 29.5, 27.6, 27.5, 27.4, 27.4, 23.0, 22.9, 14.4, 14.3 ppm. Elemental analysis: Calcd (%) for C$_{110}$H$_{162}$N$_4$: C, 85.76; H, 10.60; N, 3.64. Found: C, 85.81; H, 10.54; N, 3.67.

2,6-Bis(p-N,N-dihexylaminostyryl)-9,10-bis[(p-cyano-phenyl)ethynyl]anthracene (4c) Synthesized by the same procedure as described for **4a** except that phenyacetylene was replaced with 4-cyanophenylacetylene. The crude product was separated by column chromatography on silica gel using a hexane/CH$_2$Cl$_2$ (1:1) as the eluent. Yield, 41%; mp 191– 193 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.11 (d, J=9.0 Hz, 2H), 8.02 (s, J=3.0 Hz, 2H), 7.70 (d, J=9.0 Hz, 4H), 7.65 (d, J=9.0 Hz, 4H), 7.62 (d, J=9.0 Hz, 3.0 Hz, 2H), 7.41 (d, J= 9.0 Hz, 4H), 7.13 (d, J=16.5 Hz, 2H), 6.97 (d, J=16.5 Hz, 2H), 6.66 (d, J=9.0 Hz, 4H), 3.34 (t, J=6.0 Hz, 8H), 1.65 (m, 8H), 1.37 (m, 24H), 0.94 ppm (t, J=6.0 Hz, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.4, 136.8, 132.3, 132.2, 131.7, 130.6, 128.5, 128.4, 127.0, 124.8, 124.3, 124.1, 123.4, 118.9, 117.1, 117.1, 111.8, 111.6, 100.7, 91.4, 51.4, 32.0, 27.6, 27.1, 23.0, 14.3 ppm. Elemental analysis: Calcd (%) for C$_{72}$H$_{78}$N$_4$: C, 86.53; H, 7.87; N, 5.61. Found: C, 86.47; H, 7.85.11; N, 5.66.

Photophysical studies

All spectroscopic measurements were performed in toluene solutions (spectroscopic grade). Samples were dissolved in toluene at concentrations of 1.0×10^{-5} M and the absorption and the fluorescence spectra were recorded on a Hewlett– Packard 8453 diode array spectrophotometer, and a Amico Bowman series 2 luminescence spectrometer, respectively. The fluorescence quantum yield was determined using fluorescein, coumarine 307 or Rhodamine B as the reference according to the literature method [29].

The two-photon absorption cross-sections of **2**−**4** were determined by two-photon-induced fluorescence method using the femto-second laser pulses as reported [13, 28]. The pulse width, repetition rate of the laser and the input excitation power were 160 fs, 90 MHz, and 50 μW respectively. The experimental setup for the measurement is described in reference [28].

The fluorescence was collected with a camera lens, focused with a lens (f=120 mm, diameter=30 mm) at the entrance slit of the monochromator (TRIAX320, Jobin–

Yvon, F_{number}=4.1), and then detected by using the CCD detector system. Samples were dissolved in toluene at concentrations of 5.0×10^{-6} M and the two-photon induced fluorescence intensity was measured at 740−960 nm by using fluorescein (8.0×10^{-6} M, pH=11) as the reference, whose two-photon properties have been well documented in the literature [30]. The two-photon cross section (δ) 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 stand for the sample and reference molecules. The intensity of the signal collected by a CCD detector was denoted as S. Φ is the fluorescence quantum yield. ϕ is the overall fluorescence collection efficiency of the experimental apparatus. The number density of the molecules in solution was denoted as c. δ_r is the TPA cross section of the reference molecule.

Results and discussion

Synthesis 2,6-Dimethyl-9,10-dibromoanthracene, **1a**, **1c**, **2a**, and **2c** were available from a previous study [26]. Synthesis of other compounds are performed as in Scheme 2. Compound **2b** was prepared by the method of Suzuki coupling between **A** and *p*-didecylaminophenylbor-onic acid. To synthesize **3a**–**c**, **A** was subjected to the Heck coupling with *p*-subsituted styrenes. Compounds **4a**–**c** were synthesized by the method of Sonogashira coupling between **A** and *p*-subsituted phenylacetylenes. All compounds were unambiguously characterized by ^{1}H and ^{13}C nmr spectroscopic analysis and the results of elemental analysis.

One-photon absorption and emission spectra The one-photon absorption spectra of **1**–**4** in toluene solution are complicated and no clear trend is evident in the wave-lengths of the maximum absorption (λ_{max}) brought out by the change of the 9,10-substituents (Fig. 1). On the other hand, a reasonable correlation can be found when the longest wavelength absorption bands (λ_{CT}) are compared with the 9,10-substituents. First of all, there is modest increase in the λ_{CT} in the order, **1a** < **2a** < **3a** < **4a**, indicating a gradual increase in the extent of intramolecular charge transfer (ICT) (Table 1). Hence, the electron withdrawing ability of the 9,10-substituent seems to increase in the order, H < Ph < styryl < phenylethynyl. In addition, the spectra for **3a**–**c** are broader than those for **4a**–**c**, probably because of the steric hindrance between the vinyl groups and the anthracenyl moiety, which might have distorted the structure and increased the number of possible transition. When cyano groups are introduced at 9,10-positions, the λ_{CT} increases by more than 130 nm (**1a** vs **1c**). The effect is much smaller for **2a** and **2c** (22 nm) and for **3a** and **3c** (10 nm), indicating that the electronic effect is
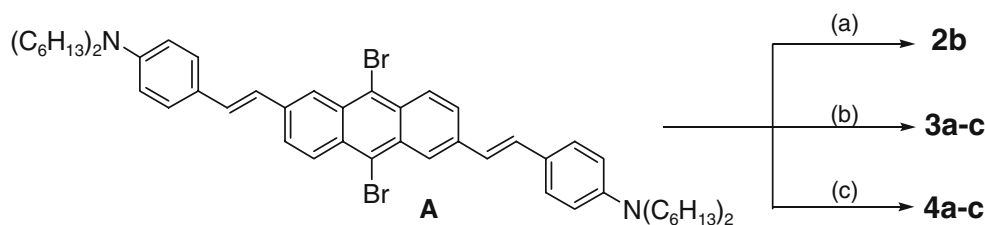
Scheme 2 Reagents and conditions: (a) p-$(C_6H_{13})_2NC_6H_4B(OH)_2$/Pd(PPh$_3$)$_4$/Na$_2CO_3$/toluene/reflux/16 h; (b) p-XC$_6$H$_4$CH=CH$_2$/ Pd(OAc)$_2$ /(o-tolyl)$_3$P/NEt$_3$/MeCN/reflux /24 h; (c) p-XC$_6$H$_4$C≡CH/Pd(PPh$_3$)$_4$/CuI/(i-Pr)$_2$NH/toluene/80 °C/12 h

reduced by the intervening phenyl and styryl groups (Table 1). Interestingly, the λ_{CT} of **4c** is shorter than that of **4a**, while the extinction coefficient is larger. This indicates that the ICT is less efficient for **4c** than **4a**, despite enhanced transition moment. On the other hand, the λ_{CT} values of **2b**, **3b**, and **4b** are very similar to those of **2a**, **3a**, and **4a**, indicating that the donor groups at 9,10-positions have little influence on the ICT (Table 1). Finally, the much smaller ε value for **2b** than others at the λ_{CT} is due to the fact that the

λ_{max} of **2b** appears at <300 nm and the absorption becomes very weak at >350 nm (Fig. 1).

In contrast to the absorption spectra, the fluorescence spectra exhibit monotonous bathochromic shift in the order, **1a** < **2a** < **3a** < **4a**, and when with increasing acceptor strength, it showed, **1a** < **1c**, **2a** < **2c**, **3a** < **3c**, **4a** < **4c** (Fig. 2 and Table 1). The abnormal behavior noted in the absorption spectra for **4a** and **4c** were not found in the
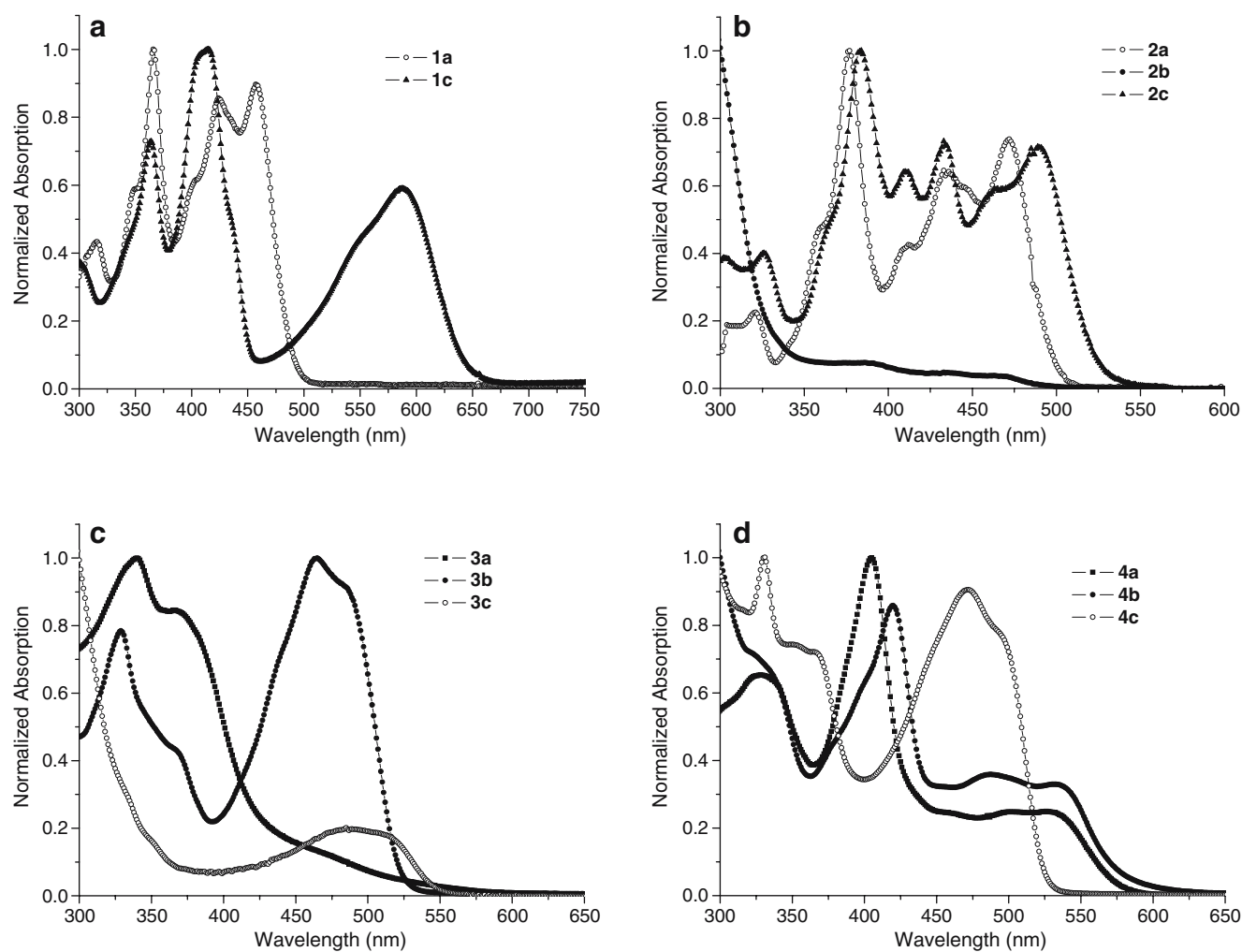
Fig. 1 Normalized absorption spectra of **2–4** (**a–d**) in toluene (at concentrations of 5.0×10^{-6} M)

Table 1 One- and two-photon properties of **1–4**

Cpd	λ_{CT} $(10^{-4}\varepsilon)^a$	$\lambda_{fl}{}^b$	$\Delta\tilde{v}{}^c$	Φ^d	$\lambda_{max}^{(2)}$ e	$\delta_{max}{}^f$	$\Phi\delta_{max}{}^g$
1a[h]	456 (6.65)	487	1,400	0.78	800	1,100	860
1c[h]	587 (4.88)	656	1,790	0.11	990	2,290	250
2a[h]	466 (4.69)	501	1,500	1.0	780 (800)[i]	770 (910)[i]	770 (910)[i]
2b	464 (0.44)	489	1,100	0.85	800	1,130	960
2c[h]	488 (4.55)	535	1,800	0.64	840 (830)[i]	1,570 (1,570)[i]	1,000(1,000)[i]
3a	485 (0.38)	545	2,270	0.12	940	1,180	140
3b	489 (2.17)	570	2,910	0.036	800	3,940	140
3c	495 (0.83)	610	3,800	0.089	820	1,870	170
4a	530 (1.67)	577	1,537	0.25	940	740	185
4b	532 (2.38)	563	1,035	0.43	800	3,010	1,290
4c	498 (4.71)	628	4,160	0.15	>960	>2,360	>350

[a] The wavelength of the longest wavelength absorption band in the one-photon absorption spectra in nm. The numbers in the parenthesis are the molar absorption coefficient in each wavelength. [b] λ_{max} of the one-photon fluorescence spectra in nm. [c] Stokes shift in cm^{-1}. [d] Fluorescence quantum yield. [e] λ_{max} of the two-photon absorption spectra in nm. [f] The peak two-photon absorption cross section in 10^{-50} cm^4 s $photon^{-1}$ (GM). The experimental uncertainty is in the order of 10–15%. [g] Two-photon action cross section. [h] The data are taken from Ref. [26]. [i] This work

emission spectra probably because the ICT is more efficient in the excited- than in the ground-state. All compounds show modest to large Stokes shifts ranging from 1,100 for **2b** to 4,160 cm^{-1} for **4c** (Table 1). The fluorescence Stokes shift increases in the order, **1a < 2a < 4a < 3a**. The larger Stokes shift for **3a** than others is due to the smaller λ_{CT} that can be attributed to the steric hindrance between the vinyl groups and the anthracenyl moiety, which may have distorted the
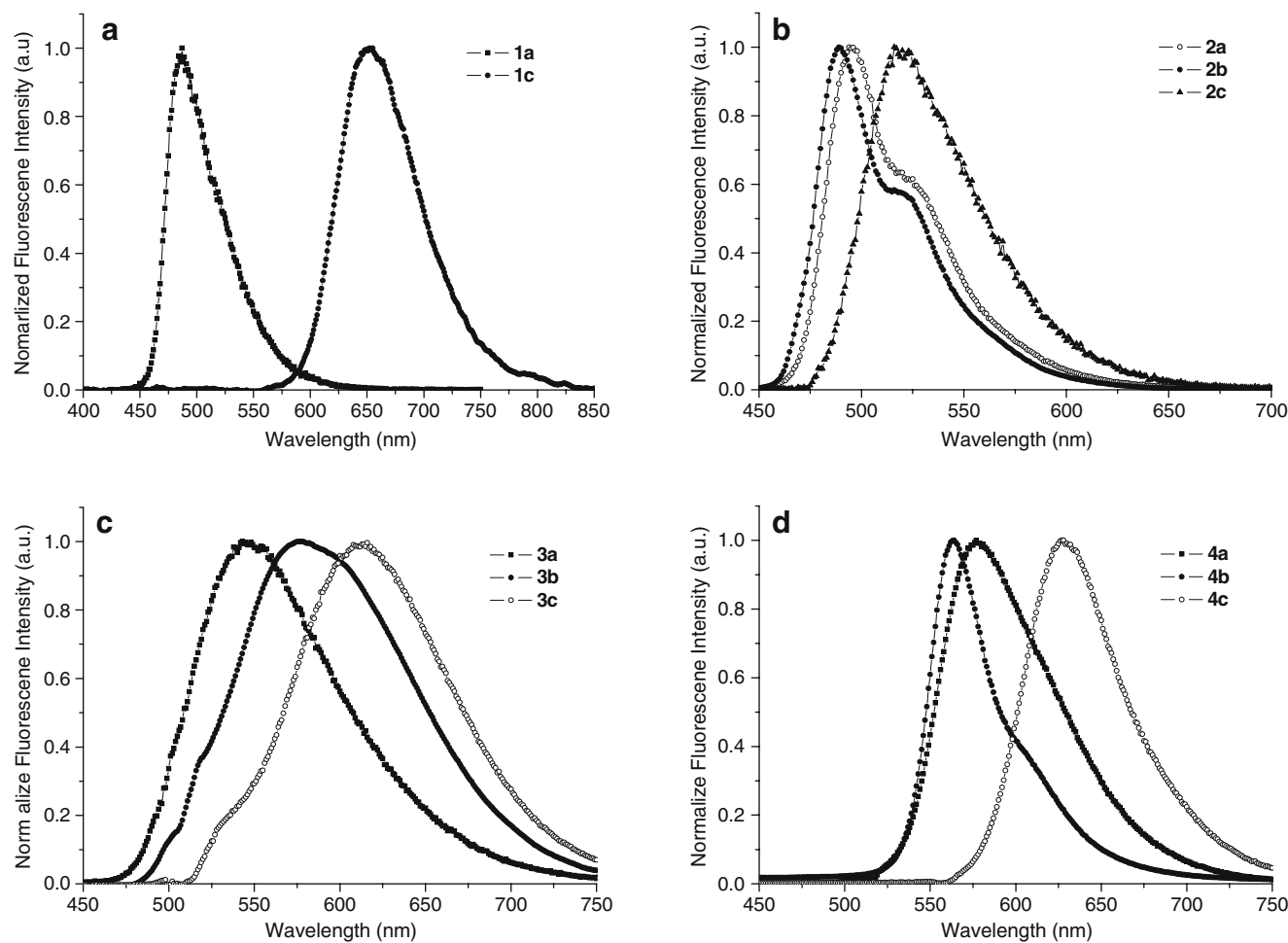

Fig. 2 Normalized fluorescence spectra of **2–4** (**a–d**) in toluene (at concentrations of 5.0×10^{-6} M)
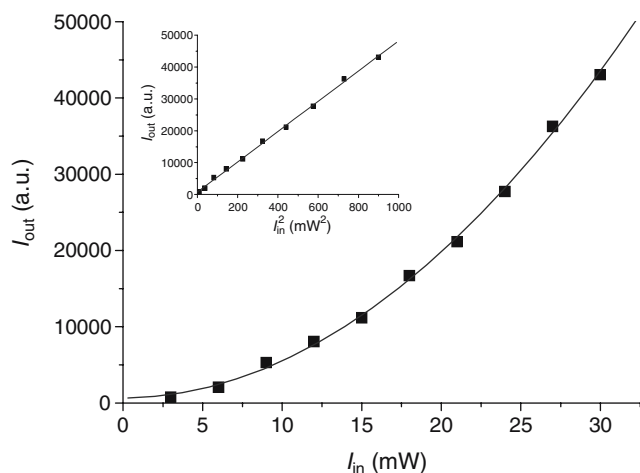
Fig. 3 Dependence of output fluorescence intensity (I_{out}) of compound **2c** in toluene on the input laser power (I_{in}). The insert shows the linear dependence of I_{out} on I_{in}^2 (Excitation wavelength=830 nm, 90 MHz, τ=160 fs)
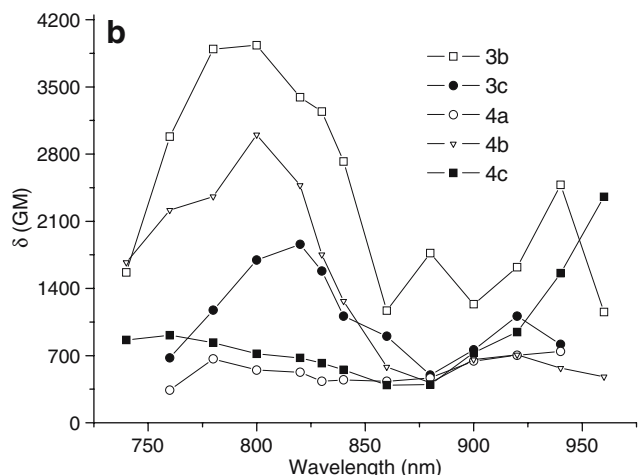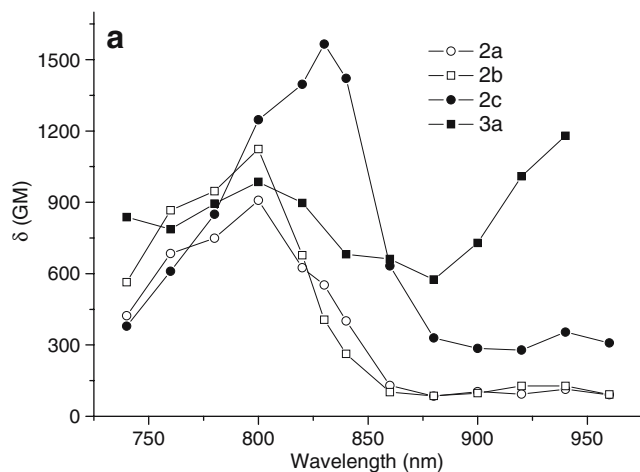
Fig. 4 Two-photon excitation spectra of **2–4** (**a–d**) in toluene (at concentrations of 5.0×10^{-6} M)
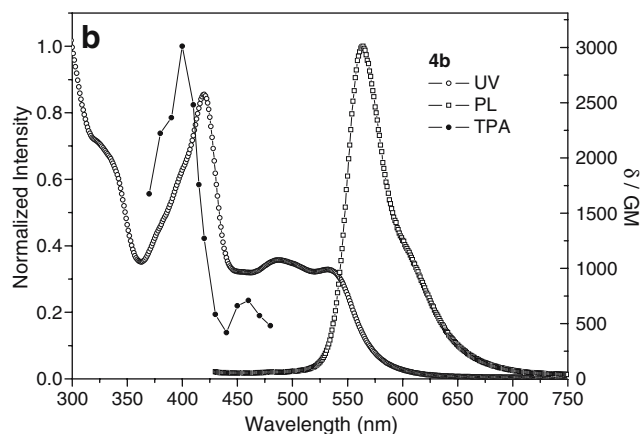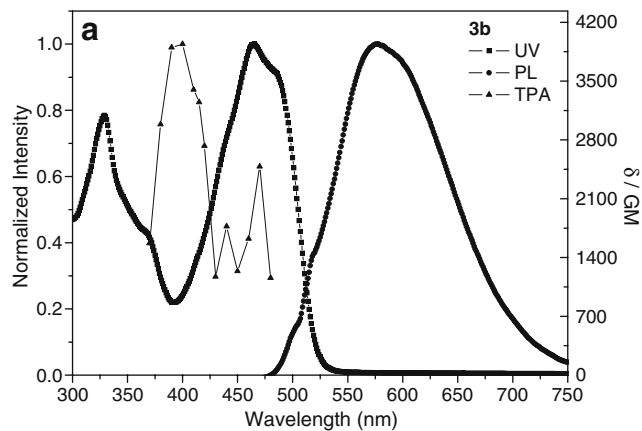
Fig. 5 One-photon absorption, fluorescence, and two-photon excitation spectra for **3b** (**a**) and **4b** (**b**) in toluene. The two-photon spectrum is plotted against half the wavelength (twice the photon energy) (at concentrations of 5.0×10^{-6} M)

structure and reduced the ICT (*vide supra*). The Stokes shift also increases as the acceptor strength increases, that is, **1a** < **1c**, **2a** < **2c**, **4a** < **4c**, indicating that the energy gap between the ground- and excited-states decreases in this order (Table 1). As the acceptor strength increases, the charge transfer character of the excited electronic state would increase. This leads to the prediction that the solvation energy of the excited electronic state becomes large and the fluorescence Stokes shift too will increase. Interestingly, the Stokes shifts of **2b** and **4b** are much smaller than those of **2a** and **4a** (Table 1). This indicates that the donors may have destabilized the emitting states more than the Franck–Condon states. For **3b**, this effect is not evident probably because of the distorted structure (vide supra). Most of the compounds are strongly fluorescent with modest to high fluorescence quantum yields. The much smaller quantum yields for **1c** and **3a–c** may be due to the lower energy of the emitting states and/or distorted structures, and thus have facilitated the nonradiative pathways.

Two-photon cross sections The two-photon cross section (δ_{TPA}) was measured by the two-photon-induced fluores-

cence measurement technique using the femto-second (fs) laser pulses as described [13, 20]. As shown in Fig. 3, the output intensity of two-photon excited fluorescence is linearly dependent on the square of the input laser intensity, thereby indicating the occurrence of nonlinear absorption.

Figure 4 shows the two-photon excited spectra of **2−4** in toluene. The values of maximum two photon cross section (δ_{max}) for **2a** and **2c** measured by the nano- and femtosecond pulses are similar within experimental error (Table 1). This result validates the comparison between earlier and the present ones.

All compounds show large two-photon cross sections in the range of 740−3,940 GM at 800−960 nm (Fig. 4). The normalized one-photon absorption, emission, and the two-photon excitation spectra for **3a** and **4b** are depicted in Fig. 5. It shows that $\lambda_{max}^{(2)}/2$ of **3a** and **4b** are located at shorter wavelengths than the absorption maxima. This is consistent with the prediction that the two-photon allowed states for the quadrupoles are at a higher energy than the one-photon allowed states [31]. Interestingly, **3a** and **4c** show appreciable two-photon absorption into the lowest excited states (>930 nm), although we cannot rule out the possibility that the real $\lambda_{max}^{(2)}$ for these compounds may exist beyond the upper limit of our experimental wavelength range (Fig. 4).

When the 9,10-substituents are varied from H (**1a**) to Ph (**2a**) to styryl (**3a**) to phenylethynyl (**4a**), the δ_{max} values are scattered in the range of 740–1,100 GM. The effect of the substituents is more evident when either donor or acceptor group is introduced at the 9,10-positions. When the donor groups are substituted at the 9,10-positions, the δ_{max} value shows parallel increase with λ_{CT} in the order, **2b** < **3b** < **4b**. A similar result is observed for compounds with acceptor groups at the 9,10-positions, that is, **2c** < **3c** < **4c** < **1c**. Moreover, the δ_{max} values of a given series of compounds are always larger with a stronger acceptor, that is, **1a** < **1c**, **2a** < **2c**, **3a** < **3c**, **4a** < **4c**. Here again, a parallel increase between the δ_{max} and λ_{CT} is observed. An exception to this trend is the larger δ_{max} for **4c** than **4a**, despite shorter λ_{CT}. At present, the origin of this dichotomy is not clear.

The most interesting result from this study is the larger δ_{max} values of the compounds having the donor groups at the 9,10-positions than those of the parent compounds, that is, **2a** < **2b**, **3a** < **3b**, **4a** < **4b**. A similar result was reported for 2,6-bis[4-(p-dialkylaminostyryl)styryl]anthracene with alkoxy groups at the 9,10-positions [28]. In case of **3b** and **4b**, the δ_{max} values are even larger than those for **3c** and **4c**. The origin of this dichotomy is not clear. However, it is interesting to note that $\lambda_{max}^{(2)}$ of these compounds are close to one of the absorption maxima (Fig. 5). The TPA cross section would increase, if the two-photon allowed states are close to the Franck–Condon

state [21]. This result underlines the importance of substituting donor groups at 9,10-positions to design more efficient two photon materials.

The values of $\Phi\delta_{max}$, the two-photon excited fluorescence (TPEF) action cross-section, are in the range of 140−1,290 GM. The small $\Phi\delta_{max}$ values of **1c**, **3a–c**, and **4a** are due to the small δ_{max} and/or low fluorescence quantum yields. From a practical perspective, **1a**, **2a–c**, and **4b** showing the largest TPEF action cross-section values are most useful for applications that use TPEF. Moreover, the $\lambda_{max}^{(2)}$ values close to 800 nm provide additional advantage because Ti/Sappier laser emits light most efficiently at this wavelength. In this respect, phenyl and phenylethynyl groups are superior to the styryl groups as the 9,10-substituents for the design of efficient two-photon materials. Moreover, the donor and acceptor groups at the 9,10-positions would further increase δ_{max}.

Conclusions

In this work, we have synthesized a series of 2,6-bis(p-dialkylaminostyryl)- anthracene derivatives having phenyl, styryl, and phenylethynyl groups at 9,10-positions (**1−4**) and measured their one- and two-photon absorption properties. In general, the λ_{CT} and λ_{fl} increases with the conjugation length and the electron withdrawing ability of the 9,10-substituent. The two photon cross sections of **1−4** are in the range of 740−3,940 GM at 780−960 nm. The value increases significantly by the donor or acceptor groups at the 9,10-positions. Moreover, Ph and phenylethynyl groups are better when compared to the styryl group at 9,10-positions in terms of the two-photon cross section. From a practical perspective, **1a**, **2a–c**, and **4b** showing the largest two-photon excited fluorescence (TPEF) action cross-section are most useful for applications that will use TPEF.

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