Two-Photon Absorption Properties of 2,6-Bis(styryl)anthracene Derivatives: Effects of Donor–Acceptor Substituents and the π Center

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Abstract: A series of 2,6- and 2,7-bis(styryl)anthracene derivatives with the donors at the styryl group and acceptors at the 9,10-positions have been synthesized, and their two-photon cross sections ($\Phi\delta_{max}$) were determined. These compounds exhibit a peak two-photon absorptivity (δ_{max}) in the range of 700–2500 GM at 780–1030 nm. Values of λ_{max} and Stokes shifts increase as the acceptor is changed to a stronger one. There is also a parallel increase in $\lambda^{(2)}_{max}$ and δ_{max} with the same variation of the chromophore structure. Both $\lambda^{(2)}_{max}$ and $\Phi\delta_{max}$ have been optimized by introducing donor-substituted styryl groups at the 2,6-positions and *p*-cyanophenyl groups at the 9,10-positions, respectively. The effect of a π center on the two-photon absorption properties has been assessed by comparing the existing data for a variety of D–π–D derivatives.

Keywords: anthracene · donor–acceptor systems · excited states · fluorescence · two-photon absorption

Introduction

The synthesis of organic materials with a large two-photon cross section is of considerable research interest owing to their potential applications in a number of new areas, including biological imaging, optical power limiting, two-photon upconversion lasing, two-photon fluorescence excitation microscopy, 3D microfabrication, and photodynamic therapy.[1–15] The most frequently investigated structural motifs for efficient two-photon absorption (TPA) chromophores are donor–bridge–acceptor (D–π–A) dipoles, donor–bridge–donor (D–π–D) quadruples, and octupoles. Such derivatives of fluorene, triphenylamine, dithienothiophene, bis(styryl)benzene, dihydrophenanthrene, tricyanobenzene, and dendrimers have been synthesized and their structure–property relationship has been investigated.[16–20] The results of these studies reveal that the TPA cross section increases with increasing donor strength, conjugation length, and planarity of the π center.

Among the most attractive π centers is the anthracene moiety, not only because it is planar, but it is also an excellent fluorophore. Moreover, anthracene derivatives have been extensively utilized as fluorescence sensors for metal ions and biological molecules.[21] Therefore, there seems to be a great potential for their development as two-photon sensors for biological applications. We recently reported that 2,6-bis(styryl)anthracene and 9,10-bis(arylethynyl)anthracene derivatives exhibit large two-photon cross sections, demonstrating the usefulness of the anthracene moiety as the π center.[20f,h] In this work, we have synthesized a series of 2,6- and 2,7-bis(styryl)anthracene derivatives (**1**–**4**; Scheme 1) and studied their one- and two-photon absorption properties (δ_{TPA}). We were interested in studying the effects of 1) changing the electron-withdrawing abilities of the 9,10-substituents, 2) changing the donors from $N(Hex)_2$ to N(*i*-amyl)tol to NPh_2, and 3) quadrupolar (**1**–**4**) and dipolar (**5**) symmetry on the one- and two-photon spectroscopic properties. Finally, the effect of changing the π center on the two-photon absorption properties was assessed by a comparison with the existing data for a variety of D–π–D derivatives.[17,19]

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. This information includes one-photon absorption, fluorescence, and two-photon excitation spectra for **1b**, **1c**, **2a**, **2b**, **2c′**, **3a**, **3b**, **3c′**, **4a**–**c**, and **5a** in toluene.

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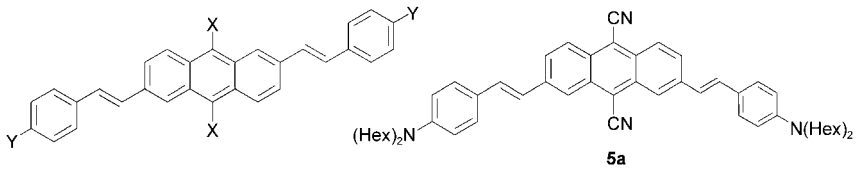
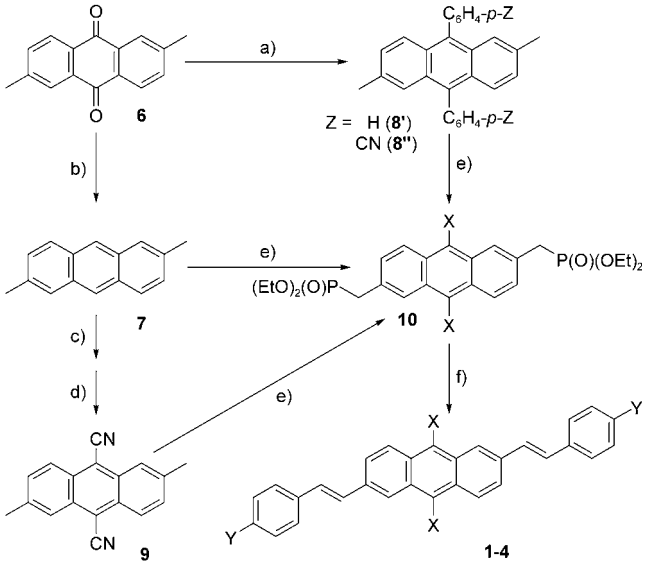


Scheme 1. The 2,6- and 2,7-bis(styryl)anthracene derivatives used in this study: X = H (**1**), Ph (**2**), *p*-CNC_6H_4 (**3**), CN (**4**); Y = $N(Hex)_2$ (**a**), NH_2 (**a′**), N(*i*-amyl)tol (**b**), $N(C_6H_4$-*p*-*t*Bu$)_2$ (**c**), NPh_2 (**c′**).

Results and Discussion

Synthesis: All of the 2,6-bis(styryl)anthracene derivatives (**1**–**4**) were synthesized from 2,6-dimethylanthraquinone (**6**) (Scheme 2).[22] Reduction of **6** with aluminum powder afforded 1,6-dimethylanthracene (**7**) in 73% yield. Bromination of **7** followed by cyanation produced 9,10-dicyano-2,6-dimethylanthracene in overall 75% yield. 2,6-Dimethyl-9,10-diphenylanthracene (**8′**) and 2,6-dimethyl-9,10-bis(*p*-cyanophenyl)anthracene (**8″**) were prepared by the reaction between **6** and PhMgBr and *p*-CNC_6H_4Li, respectively, followed by the reduction with Zn powder.



Scheme 2. Reaction conditions: a) 1. PhMgBr/THF/RT/4 h (**8′**) or *p*-CNC_6H_4Br/BuLi/THF/−78 °C to RT/5 h (**8″**); 2. Zn/AcOH/120 °C/3 h; b) $HgCl_2$/Al/CCl_4/cyclohexanol/85 °C/48 h; c) Br_2/CCl_4/0 °C/5 h; d) CuCN/pyridine/220 °C/4 h; e) 1. NBS/BPO/benzene/reflux/3 h; 2. $P(OEt)_3$/reflux/12 h; f) LDA/THF/*p*-YC_6H_4CHO/−78 °C to RT/6 h.

To prepare **10**, compounds **7**–**9** were reacted with NBS and then treated with $P(OEt)_3$. Compounds **1**–**4** were synthesized by a condensation reaction between the phosphonate ylides and the appropriate benzaldehyde derivatives (Scheme 2). The 2,7-bis(*p*-dihexylaminostyryl)anthracene derivative (**5a**) was synthesized by the same procedure as described for **4a** except that 2,7-dimethylanthraquinone was used as the starting material. The structures of **1**–**4** and **5a** were unambiguously characterized by ^1H and ^{13}C NMR spectroscopic analysis and elemental analysis.

One-photon absorption and emission spectra: Figure 1 shows the one-photon absorption spectra of solutions of **1a**–**5a** in toluene. The shapes of the spectra are similar to that of anthracene, except that the absorption maxima (λ_{max}) are shifted to a longer wavelength by the extended conjugation. For a given donor, λ_{max} increases monotonically with the electron-accepting ability of the 9,10-substitutent, that is, **1a** < **2a** < **3a** < **4a**. This indicates a gradual increase in the intramolecular charge transfer (ICT) between the donor and acceptor. Similarly, λ_{max} of **5a** is shorter than **4a**, probably because the acceptor strength is attenuated in the former by the fact that only the 9-CN group is in direct resonance with the $N(Hex)_2$ donors.

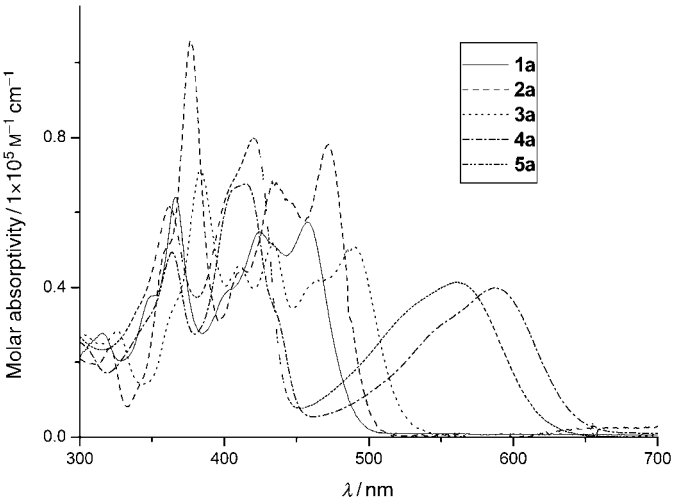


Figure 1. Molar absorption spectra for **1a**–**5a** in toluene.

When the donor is changed from $N(Hex)_2$ to N(*i*-amyl)tol to NAr_2, λ_{max} of **1a**–**c** remains nearly the same, despite the decrease in the donor strength (Table 1). It is well established that the substitution of the NPh group in a simple D–π–A conjugate system increases the π conjugation in a "nontraditional" manner, where the additional π-electron unit lies outside the donor–acceptor framework.[23] Hence, this result could be understood if the weaker donor strength is compensated for by the "nontraditional" conjugation effect of the NPh group. On the other hand, λ_{max} values of **2**–**4** decrease with a weaker donor, indicating that the special effect of the NPh group becomes less important as the ICT from the donor to the acceptor becomes more important. Moreover, the longer the λ_{max} is, the larger the blueshift caused by the change to a weaker donor is (Table 1).

The fluorescence spectra of **1a**–**5a** are shown in Figure 2. None of these spectra have multiple peaks, which indicates

Table 1. One- and two-photon properties of 2,6- and 2,7-bis(styryl)anthracene derivatives (**1**–**5**).

	λ_{max}[a]	λ^{fl}_{max}[b]	$\Delta\tilde{\nu}$[c]	Φ[d]	$\lambda^{(2)}_{max}$[e]	δ_{max}[f]	$\Phi\delta_{max}$[g]
1a	455	487	1444	0.78	800	1100	860
1b	454	483	1322	0.84	780	1080	910
1c	454	479	1450	0.82	780	1340	1100
2a	466	501	1499	1.0	780	770	770
2b	463	495	1396	1.0	780	700	700
2c′	458	481	1044	1.0	780	720	720
3a	488	535	1800	0.64	840	1570	1000
3b	482	530	1879	0.88	840	1180	1040
3c′	474	509	1451	0.84	820	1760	1480
4a	587	656	1792	0.11	990	2290	250
4b	575	643	1839	0.15	990	2210	330
4c	566	635	1920	0.15	990	2490	370
5a	562	650	2409	0.088	1030	720	60

[a] λ_{max} of the one-photon absorption spectra in nm. [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 absorptivity in GM, where 1 GM (Goppert–Mayer) $= 1\times10^{-50}\,cm^4\,s\,photon^{-1}$. [g] Two-photon action cross section in GM at $\lambda^{(2)}_{max}$.

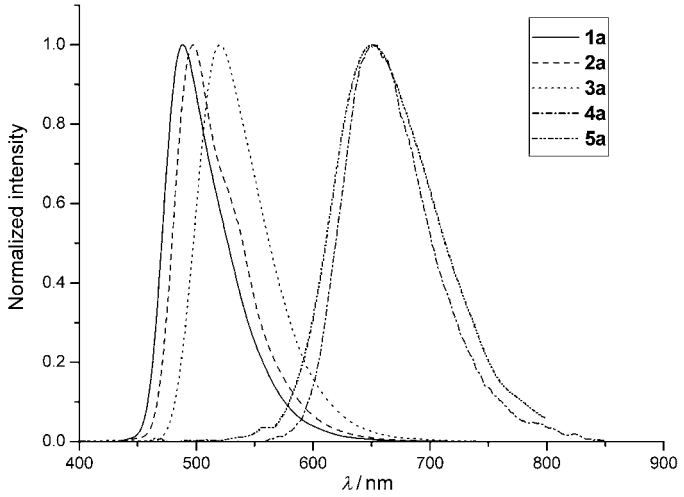


Figure 2. Normalized one-photon fluorescence spectra for **1a**–**5a** in toluene.

that the emission occurs from the lowest excited state with the largest oscillator strength. The peak positions in the absorption and fluorescence spectra are summarized in Table 1. As already noted in the absorption spectra, the fluorescence spectra exhibit a monotonous bathochromic shift with increasing acceptor strength. All compounds show large Stokes shifts ranging from 1044 to 2409 cm^{-1} for **2c′** and **5a**, respectively (Table 1). As expected, the fluorescence Stokes shift increases as the acceptor strength increases. This means that the energy gap between the ground and the excited states decreases monotonically in the order, **1a** > **2a** > **3a** > **4a** (Table 1). As the acceptor strength increases, the charge-transfer character of the excited electronic state increases. This leads to the prediction that the solvation energy of the excited electronic state becomes large and the fluorescence Stokes shift will increase too. Moreover, the Stokes shift for **5a** is much larger than that of **4a**. This is because the λ^{fl}_{max} value is almost the same for both compounds, whereas λ_{max} of **5a** is significantly blueshifted. Because the dipole moment of **5a** is larger than that of **4a**, the emitting state of the former would be more stabilized by the ICT than expected from the acceptor strength. Except for **2c′** and **3c′**, the Stokes shifts are relatively insensitive to the donors. This indicates that the effect of donors on the Franck–Condon and emitting states are similar. Most of the compounds are strongly fluorescent with high fluorescence quantum yields. The much smaller quantum yields for **4a**–**c** and **5a** may be attributable to the lower energy of the emitting states, which may facilitate nonradiative pathways. As expected, the fluorescence quantum yields are always higher when N(*i*-amyl)tol or NAr_2 is the donor.[24]

Two-photon cross sections: The two-photon cross section (δ_{TPA}) was measured by means of the two-photon-induced-fluorescence measurement technique with nanosecond laser pulses as previously reported.[17b,20b]

Figure 3 shows the two-photon excited spectra for **1a**–**5a** in toluene. All compounds show large two-photon cross sections in the range of δ_{max} = 700–2300 GM at $\lambda^{(2)}_{max}$ = 780–1030 nm. The normalized one-photon absorption, emission, and the two-photon excitation spectra for **1a** are depicted in Figure 4. The corresponding spectra for other compounds are shown in Figure S1 in the Supporting Information. The results are summarized in Table 1.

Figure 4 shows that $\lambda^{(2)}_{max}/2$ of **1a** is located at a shorter wavelength than the lowest energy absorption maximum (λ_{max}). This is consistent with the prediction that the two-photon allowed states for quadrupoles are at a higher energy than the Franck–Condon states.[25] Nevertheless, there is a significant overlap between the one- and two-photon spectra in terms of the total absorption energy. Perhaps this may be the reason why δ_{max} values for **1**–**4** are so large. In addition, compounds **3a**, **3b**, and **3c′** show appreci-

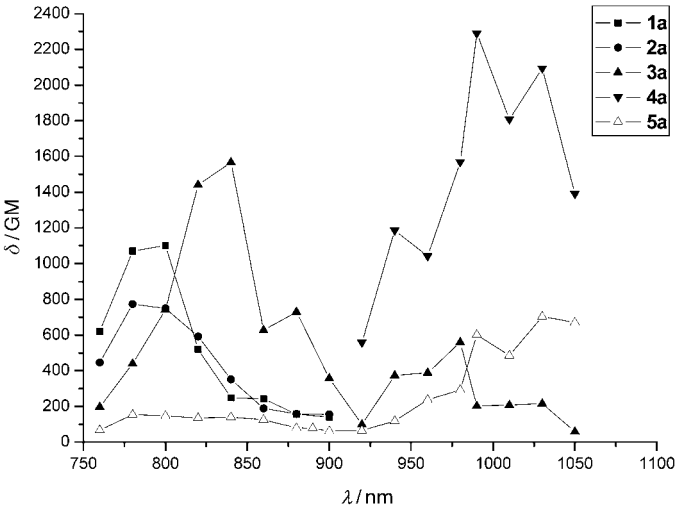


Figure 3. Two-photon spectra for **1a**–**5a** in toluene.

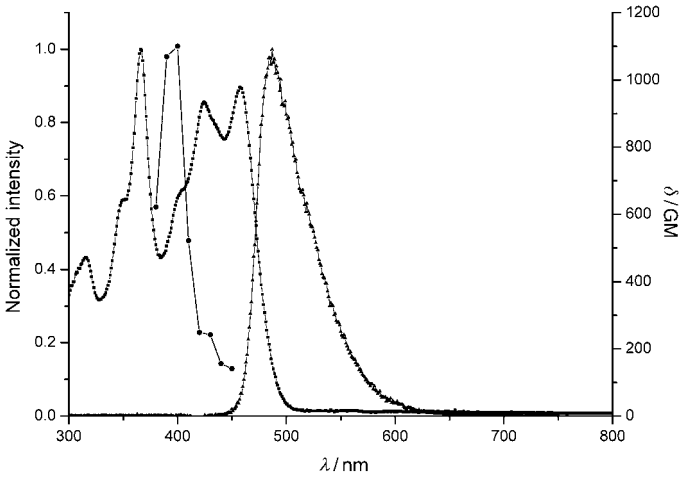


Figure 4. One-photon absorption (■), fluorescence (▲), and two-photon spectra (●) for **1a** in toluene. The two-photon spectrum is plotted against half the wavelength (twice the photon energy).

able two-photon absorption into the lowest excited states (Figure S1). Moreover, the values of $\lambda_{max}^{(2)}$ for **1**–**4** increase with the electron-withdrawing ability of the 9,10-substituents (Table 2). This indicates an interesting possibility that the wavelength of the maximum two-photon cross section could be tuned by the use of an appropriate substituent. Furthermore, the longest $\lambda_{max}^{(2)}$ is noted for **5a** at $2\lambda_{max}$, as predicted for a dipolar molecule, although we cannot rule out the possibility that the real $\lambda_{max}^{(2)}$ for **5a** may exist at a longer wavelength (Figure S1).[25] Interestingly, $\lambda_{max}^{(2)}$ for **1**–**3** appear near 800 nm (Table 2). This turns out to be important for practical applications because most of the two-photon fluorescence (TPF) microscopy uses an excitation laser with a wavelength of $\approx$800 nm.

Table 2. Effect of the π center on the two-photon absorption properties of D–π–D derivatives.

	λ_{max} [a]	λ_{max}^{fl} [b]	Φ [c]	$\lambda_{max}^{(2)}$ [d]	δ_{max} [e]	$\Phi\delta_{max}$ [f]
A1a[g,h]	410	455	0.88	730	995	880
1a[i]	455	487	0.78	800	1100	860
B1a[j,k]	465	582	0.63	795	340	530
C1a[l,m]	410	456	0.86	740	1730	1490
A1c[g,n]	411	457	0.93	745	805	750
1c[i]	454	483	0.82	780	1340	1100
A4a[g,o]	490	536	0.69	830	1750	1210
4a[i]	587	656	0.11	990	2290	250
A4c[g,p]	475	528	0.87	830	1640	1430
4c[i]	566	643	0.15	990	2490	370

[a–f] See Table 1 for the footnotes. [g] Ref. [17c]. [h] 1,4-Bis(*p*-dibutylaminostyryl)benzene. [i] This work. [j] Ref. [19a]. [k] 2,6-Bis(*p*-dibutylaminostyryl)dithienothiophene. [l] Ref. [19b]. [m] 2,7-Bis(*p*-dioctylaminostyryl)-9,10-dihydrophenanthrene. [n] [*p*-(*N*-phenyl-*N*-toly)aminostyryl]benzene. [o] 1,4-Bis(*p*-dibutylaminostyryl)-2,5-dicyanobenzene. [p] 1,4-Bis(*p*-diphenylamino)-2,5-dicyanobenzene.

The δ_{max} value of **1a** is 1100 GM at $\lambda_{max}^{(2)}$ = 800 nm. Except for **2a–c**, the δ_{max} value increases with the acceptor strength. As stated above, the acceptor group is expected to stabilize the excited state more than the ground state. This is expected to diminish the energy gap between the ground and two-photon allowed states, which would in turn increase the two-photon cross section, because the smaller the energy gap, the higher will be the excitation probability. This result underlines the importance of ICT in obtaining a TPA chromophore with a large δ_{max}. On the other hand, the values of δ_{max} for **2a–c** are smaller than those of **1a–c**, despite similar λ_{max}. When the donor is changed from $N(Hex)_2$ to N(*i*-amyl)tol to NAr_2, δ_{max} of **1a–c** increases gradually. However, no clear trend is observed for **2**–**4** with the same variation of the donors. Moreover, the δ_{max} value of **5a** is much smaller than that of **4a**. This result underlines the importance of the symmetry consideration in the design of efficient two-photon materials. A similar result has been previously reported.[17f]

The values of $\Phi\delta_{max}$, the two-photon excited fluorescence (TPEF) action cross section, increase in the order **5** < **4** < **2** < **1** < **3**. The much smaller $\Phi\delta_{max}$ values for **5a** and **4a–c** relative to those of the others is attributed to the smaller δ_{max} and/or fluorescence quantum yields. $\Phi\delta_{max}$ values were optimized by the use of *p*-cyanophenyl groups at the 9,10-positions. Hence, $\Phi\delta_{max}$ values for **3a–c** are in the range of 1000–1480 GM, which are among the largest values reported in the literature. Also, $\lambda_{max}^{(2)}$ values of **3a–c** are close to 800 nm. Therefore, **3a–c** may be useful for applications that use a Ti/sapphire laser as the excitation source. Finally, $\Phi\delta_{max}$ is usually larger when NAr_2 is used as the donor. The special effect of the NAr_2 donor has been previously reported.[23,24]

Effect of the π center: The effects of the π center on the one- and two-photon absorption properties of a variety of D–π–D derivatives are summarized in Table 2. Comparison of the data for **1** and **4** with those for the closely related 1,4-bis(styryl)benzene derivatives (**A1** and **A4**) reveals that λ_{max}, λ_{max}^{fl}, $\lambda_{max}^{(2)}$, and δ_{max} values increase significantly as the π center is changed from a phenyl to an anthryl group (Table 2).[17d] For instance, the values of λ_{max}, λ_{max}^{fl}, $\lambda_{max}^{(2)}$, and δ_{max} for **1a** are 455, 487, 800 nm, and 1100 GM, respectively, which are significantly larger than λ_{max} = 410, λ_{max}^{fl} = 455, $\lambda_{max}^{(2)}$ = 730 nm, and δ_{max} = 995 GM reported for 1,4-bis(*p*-dibutylaminostyryl)benzene (**A1a**). Essentially, the same changes can be seen if the data for **1c**, **4a**, and **4c** are compared with **A1c**, **A4a**, and **A4c** (Table 2). Whereas, the fluorescence quantum yields always decrease for the same variation of the fluorophore structure. The results can be readily attributed to the more extended conjugation by the anthryl than the phenyl group. As the conjugation length increases, the energy gap between the ground state and the one- and two-photon allowed states is expected to decrease in order to increase the λ_{max}, $\lambda_{max}^{(2)}$, and δ_{max} values (vide supra). It would also stabilize the emitting states to increase λ_{max}^{fl} and decrease the fluorescence quantum yield (vide supra).

The values of λ_{max}, λ_{max}^{fl}, and fluorescence quantum yields of phenyl (**A**) and dihydrophenanthryl (**C1a**) derivatives

are almost the same, although δ_{max} values are much larger for **C1a** than **A1a**. This may be caused by the increased molecular weight. As the molecular size increases, the density of states will increase, providing more effective coupling channels between the ground and two-photon allowed states, which would in turn increase the TPA cross section. On the other hand, when anthryl and dithienothienyl groups are used as the π center, both λ_{max} and λ_{max}^{fl} increase significantly and the fluorescence quantum yields decrease. This indicates the efficiency of these groups in facilitating intramolecular change transfer from the donor to the π center.

From a practical perspective, the anthracene derivatives (**1**–**4**) are advantageous for applications that utilize the two-photon absorption because $\lambda_{max}^{(2)}$ are in the range of 780–990 nm and δ_{max} values are larger. On the other hand, 1,4-bis(styryl)benzene derivatives (**A1** and **A4**) may be more useful for applications where the two-photon excited fluorescence ($\Phi\delta_{max}$) is important.

Conclusion

Herein, the TPA properties of a series of 2,6- and 2,7-bis-(styryl)anthracene derivatives have been investigated. Overall, a parallel increase in λ_{max}, λ_{max}^{fl}, $\lambda_{max}^{(2)}$, and δ_{max} values with the donor–acceptor strength is observed, although 2,7-derivatives have significantly smaller δ_{max} values. All compounds exhibit large two-photon cross sections that are useful for a variety of applications mentioned in the Introduction. Moreover, the values of λ_{max}, λ_{max}^{fl}, $\lambda_{max}^{(2)}$, and δ_{max} increased significantly on changing the π center from a phenyl to an anthryl group. This result underlines the usefulness of an anthryl group as the π center for the design of efficient two-photon fluorophores.

Experimental Section

Synthesis of 2,6-bis(styryl)anthracene derivatives

2,6-Dimethylanthracene (7): A mixture of Al powder (8.5 g, 0.31 mol), $HgCl_2$ (0.17 g, 0.63 mmol), cyclohexanol (250 mL), and CCl_4 (1.7 mL) was heated under Ar for 4 h at 85 °C and then for 12 h at 160 °C. To this flask, 2,6-dimethylanthraquinone (**6**, 6.0 g, 25 mmol) was added and the mixture was refluxed for 48 h. The solvent was removed in vacuo, and the product was purified by column chromatography (silica gel, hexane/dichloromethane 20:1). Yield: 3.8 g (73 %); m.p. 235–237 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.24 (s, 2H), 7.86 (d, J = 9.0 Hz, 2H), 7.71 (s, 2H), 7.25 (d, J = 9.0 Hz, 2H), 2.52 ppm (s, 6H; CH_3).

2,6-Dimethyl-9,10-diphenylanthracene (8′): PhMgBr (1.0 M in THF, 51 mL) was added to a solution of **6** (4.0 g, 17 mmol) in THF (150 mL) at RT. After stirring for 4 h at RT, the solution was poured into water. The solvent was evaporated, and the product was extracted with CH_2Cl_2. The resulting solution was evaporated, and acetic acid (80 mL) was added. The residue in acetic acid was heated to 120 °C, and zinc powder (6.0 g) was added in small portions over a period of 30 min. After continuous stirring for 3 h at 120 °C, the mixture was cooled to RT, poured into water, and extracted with CH_2Cl_2. The solvent was evaporated and the product was purified by column chromatography (silica gel, hexane). Yield: 2.2 g (30 %); m.p. 234–236 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.59 (m, 4H), 7.56 (m, 4H), 7.46 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.40 (s, 2H), 7.14 (d, J = 9.0 Hz, 2H), 2.38 ppm (s, 6H; CH_3).

2,6-Dimethyl-9,10-di(*p*-cyanophenyl)anthracene (8″): BuLi (1.6 M in hexanes, 14 mL, 22 mmol) was added to a two-necked flask containing anhydrous THF (40 mL) under Ar. After cooling the solution to −78 °C, a solution of *p*-cyanobromobenzene (4.6 g, 25 mmol) in THF (20 mL) was added by means of a syringe. The solution was stirred for 1 h, and **6** (2.0 g, 8.5 mmol in 40 mL THF) was slowly added. The mixture was stirred (1. 1 h at −78 °C, 2. 4 h at RT), poured into water, and extracted with CH_2Cl_2. The solvent was evaporated and acetic acid (80 mL) was added. The resulting solution was heated to 120 °C, and zinc powder (6.0 g) was added in small portions over a period of 30 min. After continuous stirring for 3 h at 120 °C, the mixture was cooled to RT, poured into water, and extracted with CH_2Cl_2. The solvent was evaporated and the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 1:1). Yield: 1.9 g (56 %); m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.93 (d, J = 9.0 Hz, 4H), 7.58 (d, J = 9.0 Hz, 4H), 7.42 (d, J = 9.0 Hz, 2H), 7.25 (s, 2H), 7.20 (d, J = 9.0 Hz, 2H), 2.40 ppm (s, 6H, CH_3).

Dimethyl-9,10-dibromoanthracene: Bromine (1.1 mL, 21 mmol) was slowly added through a dropping funnel into a solution of 2,6-dimethylanthracene (2.0 g, 9.7 mmol) in CCl_4 (200 mL) at 0 °C. The solution was stirred for 5 h at 0 °C, and aqueous sodium hydrosulfite (20 %, 50 mL) was added. The organic layer was separated and washed with water, and the solvent was evaporated to obtain 2,6-dimethyl-9,10-dibromoanthracene. Yield: 3.2 g (91 %); m.p. 188–190 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.44 (d, J = 9.0 Hz, 2H), 8.29 (s, 2H), 7.42 (d, J = 9.0 Hz, 2H), 2.61 ppm (s, 6H; CH_3).

2,6-Dimethyl-9,10-dicyanoanthracene (9): 2,6-Dimethyl-9,10-dibromoanthracene (1.8 g, 5.0 mmol), pyridine (4.0 mL), and CuCN (0.98 g, 11 mmol) were added to a pressure tube with a plunger valve and a magnetic bar under Ar. The tube was heated at 220 °C for 4 h. The mixture was cooled to room temperature and then poured with vigorous stirring into methanol. The precipitate that formed was collected on a filter paper and washed with methanol. The crude product was separated by column chromatography (silica gel, CH_2Cl_2). Yield: 1.1 g (82 %); m.p. 292–294 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.36 (d, J = 9.0 Hz, 2H), 8.22 (s, 2H), 7.64 (d, J = 9.0 Hz, 2H), 2.67 ppm (s, 6H; CH_3).

2,6-Bis[(diethoxyphosphoryl)methyl]anthracene (10′): A mixture of **7** (1.5 g, 7.3 mmol), NBS (2.7 g, 15 mmol), and benzoyl peroxide (71 mg, 0.29 mmol) in benzene (100 mL) was refluxed for 3 h. The mixture was poured into methanol, and the precipitate that collected was dried by vacuum. This intermediate was added to $P(OEt)_3$ (50 mL), and the resulting solution was refluxed for 12 h. The solvent was removed in vacuo, and the residue was purified by column chromatography (silica gel, ethyl acetate/CH_2Cl_2 2:1). Yield: 1.9 g (53 %); m.p. 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.34 (s, 2H), 7.96 (d, J = 9.0 Hz, 2H), 7.88 (s, 2H), 7.44 (d, J = 9.0 Hz, 2H), 4.04 (m, 8H; OCH_2), 3.36 (d, J = 21 Hz, 4H; $ArCH_2P$), 1.25 ppm (t, J = 7.5 Hz, 12H; CH_3).

Synthesis of phosphonate derivatives 10″–10‴′: These derivatives were synthesized from **8′**, **8″**, and **9** by the same procedure as described for **10′**.

*2,6-Bis[(diethoxyphosphoryl)methyl]-9,10-diphenylanthracene (**10″**)*: Yield: 62 %; m.p. 180–182 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.62 (d, J = 9.0 Hz, 4H), 7.57 (d, J = 9.0 Hz, 4H), 7.53 (s, 2H), 7.46 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.30 (d, J = 9 Hz, 2H), 3.97 (m, 8H; OCH_2), 3.19 (d, J = 21 Hz, 4H; $ArCH_2P$), 1.19 ppm (t, J = 7.5 Hz, 12H; CH_3).

*2,6-Bis[(diethoxyphosphoryl)methyl]-9,10-bis(p-cyanophenyl)anthracene (**10‴**)*: Yield: 49 %; m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.94 (d, J = 9.0 Hz, 4H), 7.59 (d, J = 8.5 Hz, 4H), 7.50 (d, J = 9.0 Hz, 2H), 7.40 (s, 2H), 7.35 (d, J = 9 Hz, 2H), 3.99 (m, 8H; OCH_2), 3.19 (d, J = 24 Hz, 4H; $ArCH_2P$), 1.21 ppm (t, J = 7.5 Hz, 12H; CH_3).

*2,6-Bis[(diethoxyphosphoryl)methyl]-9,10-dicyanoanthracene (**10‴′**)*: Yield: 44 %; m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.46 (d, J = 9.0 Hz, 2H), 8.35 (s, 2H), 7.83 (d, J = 9.0 Hz, 2H), 4.10 (m, 8H; OCH_2), 3.45 (d, J = 24 Hz, 4H; $ArCH_2P$), 1.30 ppm (t, J = 7.5 Hz, 12H; CH_3).

2,6-Bis(*p*-dihexylaminostyryl)anthracene (1a): LDA (1.5 M in cyclohexane, 0.34 mL, 0.51 mmol) was added dropwise to a stirred solution of **10′** (100 mg, 0.21 mmol) in anhydrous THF (15 mL) at −78 °C under Ar. The mixture was stirred for 1 h, and then 4-(*N*,*N*-dihexylamino)benzaldehyde (150 mg, 0.52 mmol) in THF (5 mL) was added dropwise over a period of 10 min. After the mixture was stirred for 2 h at −78 °C and for 6 h at RT, water (1 mL) was added and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 and washed several times with water. The solvent was evaporated, and the crude product was separated by column chromatography (silica gel, hexane/CH_2Cl_2 3:1–1:1). Yield: 58 mg (37 %); m.p. 182–184 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.27 (s, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.85 (s, 2H), 7.74 (d, J = 9.0 Hz, 2H), 7.44 (d, J = 7.5 Hz, 4H), 7.18 (d, J = 16.5 Hz, 2H), 7.08 (d, J = 16.5 Hz, 2H), 6.65 (d, J = 7.5 Hz, 4H), 3.30 (t, J = 7.5 Hz, 8H; NCH_2), 1.61 (m, 8H), 1.31 (m, 24H), 0.92 ppm (t, J = 6.0 Hz, 12H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.09, 135.31, 132.23, 131.65, 129.40, 128.52, 128.09, 125.86, 124.79, 124.12, 123.42, 111.88, 100.17, 51.33, 31.98, 27.55, 27.10, 22.94, 14.30 ppm; elemental analysis calcd (%) for $C_{54}H_{72}N_2$: C 86.57, H 9.69, N 3.74; found: C 86.59, H 9.68, N 3.68.

2,6-Bis{4-[*N*-isoamyl-*N*-(*p*-tolyl)amino]styryl}anthracene (1b): Synthesized by the same procedure as described for **1a** from **10′** and the appropriate benzaldehyde. Yield: 42 %; m.p. 210–212 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.28 (s, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.87 (s, 2H), 7.74 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 9.0 Hz, 4H), 7.20 (d, J = 16 Hz, 2H), 7.16 (d, J = 9.0 Hz, 4H), 7.12 (d, J = 16 Hz, 2H), 7.06 (d, J = 9.0 Hz, 4H), 6.82 (d, J = 9.0 Hz, 4H), 3.71 (t, J = 7.5 Hz, 4H; NCH_2), 2.36 (s, 6H; tolyl-CH_3), 1.62 (m, 6H), 0.94 ppm (d, J = 6.0 Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.43, 145.09, 135.08, 133.51, 132.25, 131.74, 130.41, 129.11, 128.64, 128.05, 127.74, 126.38, 126.06, 125.63, 125.06, 123.37, 116.97, 51.10, 36.36, 26.59, 22.91, 21.15 ppm; elemental analysis calcd (%) for $C_{54}H_{56}N_2$: C 88.48, H 7.70, N 3.82; found: C 88.49, H 7.80, N 3.77.

2,6-Bis{[4-*N*,*N*-di(*p*-*tert*-butylphenyl)amino]styryl}anthracene (1c): Synthesized by the same procedure as described for **1a** from **10′** and the appropriate benzaldehyde. Yield: 56 %; m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.28 (s, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.88 (s, 2H), 7.73 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 9.0 Hz, 4H), 7.28 (d, J = 9.0 Hz, 8H), 7.18 (m, 4H), 7.06 (d, J = 9.0 Hz, 12H), 1.32 ppm (s, 36H; *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.04, 146.16, 145.00, 134.89, 132.24, 131.78, 130.88, 128.88, 128.71, 127.52, 126.91, 126.77, 126.31, 126.19, 124.41, 123.34, 122.85, 34.56, 31.68 ppm; elemental analysis calcd (%) for $C_{70}H_{72}N_2$: C 89.31, H 7.71, N 2.98; found: C 89.24, H 7.82, N 2.94.

2,6-Bis(4-dihexylaminostyryl)-9,10-diphenylanthracene (2a): Synthesized by the same procedure as described for **1a** from **10″** and the appropriate benzaldehyde. Yield: 46 %; m.p. 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.60 (m, 10H), 7.51 (d, J = 9.0 Hz, 2H), 7.50 (d, J = 9.0 Hz, 2H), 7.49 (s, 2H), 7.33 (d, J = 9.0 Hz, 4H), 7.00 (d, J = 15 Hz, 2H), 6.89 (d, J = 15 Hz, 2H), 6.57 (d, J = 9 Hz, 4H), 3.26 (t, J = 7.5 Hz, 8H; NCH_2), 1.57 (m, 8H), 1.31 (m, 24H), 0.90 ppm (t, J = 6.0 Hz, 12H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.02, 139.38, 136.77, 134.86, 131.66, 130.42, 129.79, 129.30, 128.66, 128.05, 127.62, 127.40, 125.14, 124.73, 124.30, 122.54, 111.80, 51.29, 31.96, 27.51, 27.06, 22.92, 14.29 ppm; elemental analysis calcd (%) for $C_{66}H_{80}N_2$: C 87.95, H 8.95, N 3.11; found: C 87.99, H 8.85, N 3.03.

2,6-Bis{4-[*N*-isoamyl-*N*-(*p*-tolyl)amino]styryl}-9,10-diphenylanthracene (2b): Synthesized by the same procedure as described for **1a** from **10″** and the appropriate benzaldehyde. Yield: 38 %; m.p. 260–262 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.61 (m, 10H), 7.51 (d, J = 9.0 Hz, 2H), 7.50 (d, J = 9.0, 2H), 7.49 (s, 2H), 7.32 (d, J = 9.0 Hz, 4H), 7.12 (d, J = 9.0 Hz, 4H), 7.03 (d, J = 15 Hz, 2H), 7.01 (d, J = 9.0 Hz, 4H), 6.94 (d, J = 15 Hz, 2H), 6.76 (d, J = 9.0 Hz, 4H), 3.68 (t, J = 7.5 Hz, 4H; NCH_2), 2.34 (s, 6H; tolyl-CH_3), 1.54 (m, 6H), 0.92 ppm (d, J = 9.0 Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.27, 148.27, 145.04, 139.23, 136.97, 134.62, 133.36, 131.62, 130.43, 130.35, 129.87, 129.00, 128.70, 128.01, 127.68, 127.44, 125.81, 125.65, 124.85, 122.48, 116.96, 51.05, 36.27, 26.54, 22.86, 21.11 ppm; elemental analysis calcd (%) for $C_{66}H_{64}N_2$: C 89.55, H 7.29, N 3.16; found: C 89.58, H 7.21, N 3.15.

2,6-Bis(4-diphenylaminostyryl)-9,10-diphenylanthracene (2c′): Synthesized by the same procedure as described for **1a** from **10″** and the appropriate benzaldehyde. Yield: 51 %; m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.62 (m, 10H), 7.55 (s, 2H), 7.51 (d, J = 9.0, 2H), 7.50 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 9.0 Hz, 4H), 7.25 (m, 8H), 7.10 (m, 4H), 7.07 (d, J = 15 Hz, 2H), 7.05 (d, J = 15 Hz, 2H), 7.03 (d, J = 9 Hz, 8H), 7.01 ppm (d, J = 9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.72, 147.58, 139.10, 137.21, 134.53, 134.37, 131.75, 131.58, 130.48, 130.00, 129.48, 128.73, 128.65, 127.79, 127.69, 127.63, 126.20, 124.70, 123.75, 123.25, 122.48 ppm; elemental analysis calcd (%) for $C_{66}H_{48}N_2$: C 91.21, H 5.57, N 3.22; found: C 91.22, H 5.60, N 3.20.

2,6-Bis(4-dihexylaminostyryl)-9,10-bis(*p*-cyanophenyl)anthracene (3a): Synthesized by the same procedure as described for **1a** from **10‴** and the appropriate benzaldehyde. Yield: 53 %; m.p. 244–242 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.96 (d, J = 9.0 Hz, 4H), 7.65 (d, J = 9.0 Hz, 2H), 7.62 (d, J = 9.0 Hz, 4H), 7.44 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 9.0 Hz, 4H), 7.30 (s, 2H), 7.02 (d, J = 16.5 Hz, 2H), 6.86 (d, J = 16.5 Hz, 2H), 6.58 (d, J = 9.0 Hz, 4H), 3.27 (t, J = 6.5 Hz, 8H; NCH_2), 1.58 (m, 8H), 1.31 (m, 24H), 0.90 ppm (t, J = 6.0 Hz, 12H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.27, 144.48, 135.77, 135.05, 132.67, 132.49, 130.35, 129.86, 129.18, 128.23, 126.62, 124.19, 123.99, 123.56, 123.34, 119.21, 111.96, 111.75, 51.27, 31.95, 27.49, 27.05, 22.92, 14.30 ppm; elemental analysis calcd (%) for $C_{72}H_{70}N_4$: C 87.23, H 7.12, N 5.65; found: C 87.31, H 7.13, N 5.56.

2,6-Bis{4-[*N*-isoamyl-*N*-(*p*-tolyl)amino]styryl}-9,10-bis(*p*-cyanophenyl)anthracene (3b): Synthesized by the same procedure as described for **1a** from **10‴** and the appropriate benzaldehyde. Yield: 49 %; m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.96 (d, J = 9.0 Hz, 4H), 7.66 (d, J = 9.0 Hz, 2H), 7.62 (d, J = 9.0, 4H), 7.46 (d, J = 9.0 Hz, 2H), 7.33 (s, 2H), 7.32 (d, J = 9.0 Hz, 4H), 7.15 (d, J = 7.5 Hz, 4H), 7.04 (d, J = 15 Hz, 2H), 7.02 (d, J = 9.0 Hz, 4H), 6.90 (d, J = 15 Hz, 2H), 6.74 (d, J = 9.0 Hz, 4H), 3.68 (t, J = 9.0 Hz, 4H; NCH_2), 2.35 (s, 6H; tolyl-CH_3), 1.58 (m, 6H), 0.92 ppm (t, J = 6.0 Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.65, 144.83, 144.34, 135.57, 135.24, 133.89, 132.70, 132.46, 130.43, 130.10, 129.88, 129.27, 127.84, 127.22, 126.73, 125.39, 124.78, 124.45, 123.54, 119.15, 116.40, 112.05, 51.06, 36.27, 26.53, 22.85, 21.14 ppm; elemental analysis calcd (%) for $C_{72}H_{70}N_4$: C 87.23, H 7.12, N 5.65; found: C 87.384, H 6.89, N 5.72.

2,6-Bis(4-diphenylaminostyryl)-9,10-bis(*p*-cyanophenyl)anthracene (3c′): Synthesized by the same procedure as described for **1a** from **10‴** and the appropriate benzaldehyde. Yield: 38 %; m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.94 (d, J = 9.0 Hz, 6H), 7.80 (d, J = 9.0 Hz, 6H), 7.74 (d, J = 9.0 Hz, 6H), 7.62 (d, J = 9.0 Hz, 6H), 7.56 (s, 3H), 7.48 (d, J = 9.0 Hz, 6H), 7.22 (d, J = 15 Hz, 3H), 7.14 (d, J = 9.0 Hz, 6H), 7.06 ppm (d, J = 15 Hz, 3H); elemental analysis calcd (%) for $C_{72}H_{70}N_4$: C 87.23, H 7.12, N 5.65; found: C 87.38, H 7.04, N 5.58.

2,6-Bis(4-dihexylaminostyryl)-9,10-dicyanoanthracene (4a): Synthesized by the same procedure as described for **1a** from **10⁗** and the appropriate benzaldehyde. Yield: 51 %; m.p. 208–210 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.26 (d, J = 9.0 Hz, 2H), 8.10 (s, 2H), 7.94 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 9.0 Hz, 4H), 7.24 (d, J = 15 Hz, 2H), 7.00 (d, J = 15 Hz, 2H), 6.62 (d, J = 9.0 Hz, 4H), 3.29 (t, J = 7.5 Hz, 8H; NCH_2), 1.61 (m, 8H), 1.34 (m, 24H), 0.92 ppm (t, J = 6.0 Hz, 12H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.18, 145.65, 136.15, 132.69, 132.12, 130.56, 129.38, 128.76, 126.21, 125.04, 124.65, 123.77, 112.65, 101.45, 51.25, 31.93, 27.44, 27.03, 22.91, 14.30 ppm; elemental analysis calcd (%) for $C_{56}H_{70}N_4$: C 84.16, H 8.83, N 7.01; found: C 83.94, H 8.66, N 6.90.

2,6-Bis{4-[*N*-isoamyl-*N*-(*p*-tolyl)amino]styryl}-9,10-dicyanoanthracene (4b): Synthesized by the same procedure as described for **1a** from **10⁗** and the appropriate benzaldehyde. Yield: 47 %; m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.25 (d, J = 9.0 Hz, 2H), 8.08 (s, 2H), 7.90 (d, J = 9.0, 2H), 7.37 (d, J = 7.5 Hz, 4H), 7.23 (d, J = 16 Hz, 2H), 7.20 (d, J = 9.0 Hz, 4H), 7.07 (d, J = 9.0 Hz, 4H), 7.00 (d, J = 16 Hz, 2H), 6.74 (d, J = 9.0 Hz, 4H), 3.70 (t, J = 7.5 Hz, 4H; NCH_2), 2.38 (s, 6H; tolyl-CH_3), 1.62 (m, 6H), 0.94 ppm (d, J = 9.0 Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.25, 144.54, 139.16, 134.55, 132.74, 132.13, 132.01, 130.57, 128.40, 127.69, 126.22, 126.04, 122.98, 122.46, 116.46, 115.64, 109.65, 106.90, 51.13, 36.26, 26.57, 22.88, 21.23 ppm; elemental

analysis calcd (%) for $C_{56}H_{54}N_4$: C 85.89, H 6.95, N 7.15; found: C 86.14, H 6.82, N 7.09.

2,6-Bis{[4-*N*,*N*-di(*p*-*tert*-butylphenyl)amino]styryl}-9,10-dicyanoanthracene (4c): Synthesized by the same procedure as described for **1a** from **10′** and the appropriate benzaldehyde. Yield: 44%; m.p. >300°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=8.34 (d, J=9.0 Hz, 2H), 8.21 (s, 2H), 8.00 (d, J=9.0 Hz, 2H), 7.43 (d, J=7.5 Hz, 4H), 7.30 (d, J=7.5 Hz, 8H), 7.16 (m, 4H), 7.06 (d, J=7.5 Hz, 12H), 1.34 ppm (s, 36H; *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$): δ=149.05, 146.69, 139.16, 132.40, 132.23, 129.34, 128.13, 127.94, 126.43, 126.34, 124.87, 124.53, 123.04, 121.99, 116.88, 114.26, 110.10, 106.90, 34.60, 31.67 ppm; elemental analysis calcd (%) for $C_{72}H_{70}N_4$: C 87.23, H 7.12, N 5.65; found: C 87.27, H 7.15, N 5.58.

2,7-Bis(4-dihexylaminostyryl)-9,10-dicyanoanthracene (5a): The 2,7-bis(*p*-dihexylaminostyryl)anthracene derivative (**5a**) was synthesized by the same procedure as described for **4a** except that 2,7-dimethylanthraquinone was used as the starting material. Yield: 55%; m.p. 161–162°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=8.30 (d, J=9.0 Hz, 2H), 8.21 (s, 2H), 7.96 (d, J=9.0 Hz, 2H), 7.45 (d, J=6.0 Hz, 4H), 7.28 (d, J=18 Hz, 2H), 7.05 (d, J=15 Hz, 2H), 6.63 (d, J=9.0 Hz, 4H), 3.29 (t, J=7.5 Hz, 8H; NCH_2), 1.61 (m, 8H), 1.35 (m, 24H), 0.92 ppm (t, J=6.0 Hz, 12H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=152.28, 148.81, 140.09, 139.99, 133.66, 128.83, 127.37, 126.23, 124.74, 123.59, 121.87, 111.76, 106.40, 51.31, 31.97, 27.55, 27.08, 22.95, 14.32 ppm; elemental analysis calcd (%) for $C_{56}H_{70}N_4$: C 84.16, H 8.83, N 7.01; found: C 83.78, H 8.91, N 6.83.

Spectroscopic measurements: All spectroscopic measurements were performed with sample solutions in toluene (spectroscopic grade, Aldrich). 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 with fluorescein, coumarine 307 or Rhodamine B as the reference by the literature method.[26]

The two-photon absorption cross section of **1**–**5** was measured with the two-photon-induced fluorescence method that employed nanosecond laser pulses and Equation (1):

$$\delta = \frac{S_S \Phi_r \phi_r c_r}{S_r \Phi_S \phi_S c_S} \delta_r \qquad (1)$$

in which the subscripts s and r represent the sample and reference molecules.[17b,20b] The intensity of the signal collected by a PMT 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. Samples were dissolved in toluene at concentrations of 1.0×10^{-5} M and the two-photon-induced-fluorescence intensity was measured at 750–1050 nm. The reference standards (r) used were fluorescein (8×10^{-5} M in water, pH 11), coumarin 307 (1×10^{-5} M in MeOH), and Rhodamine B (1×10^{-5} M in MeOH), whose two-photon properties have been well characterized in the literature.[27] The intensities of the two-photon-induced fluorescence spectra of the reference and sample emitted at the same excitation wavelength were determined. The TPA cross section was calculated according to Equation (1).

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