

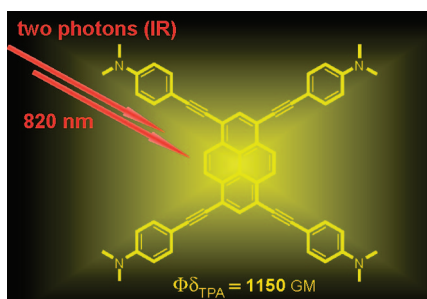
## Two-Photon Absorption Properties of Alkynyl-Conjugated Pyrene Derivatives

Hwan Myung Kim,<sup>†</sup> Yeon Ok Lee,<sup>†</sup> Chang Su Lim,  
Jong Seung Kim,\* and Bong Rae Cho\*

Department of Chemistry, Korea University,  
Seoul 136-701, Korea

jongskim@korea.ac.kr; cho@korea.ac.kr

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A series of pyrene derivatives having 4-(*N,N*-dimethylamino)phenylethynyl groups as the substituent (**1–5**) have been synthesized and their two-photon absorption properties were investigated. Comparison of two-photon cross section ( $\delta_{\max}$ ) with related compounds reveals that pyrene is as efficient a  $\pi$ -center as anthracene in two-photon materials. Moreover, the two-photon cross section ( $\delta_{\max}$ ) increased with the number of substituents reaching at the maximum value of 1150 GM for the tetra-substituted derivative (**5**). Furthermore, the two-photon action cross section ( $\Phi\delta_{\max}$ ) of **5** is comparable to that the most efficient two-photon materials. This result provides a useful guideline to the design of efficient two-photon materials bearing pyrene as a  $\pi$ -center.

Much effort has been devoted to develop organic materials exhibiting large two-photon absorption (TPA) cross sections ( $\delta$ ) because they can be excited upon irradiation of low-energy photons and emit a light that is blue-shifted.<sup>1–5</sup> This can ensure longer penetration depth, reduction of photodamage, and photobleaching useful for practical applications such as photodynamic therapy,<sup>6</sup> three-dimensional imaging,<sup>7</sup> and two-photon microscopy.<sup>8</sup> The results of structure–property relationship

\* Corresponding authors.

<sup>†</sup> These authors contributed equally to this work.

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studies reveal that the TPA cross sections ( $\delta$ ) increase with the donor–acceptor strength, conjugation length, and planarity of the  $\pi$ -center.

The most attractive  $\pi$ -center for two-photon materials is the pyrene moiety because it not only is planar but also has been extensively studied in various areas of chemical biology as a fluorophore by introducing appropriate structural modification. Due to its durable electronic properties, its derivatives have also been used in many applications including microenvironment sensors,<sup>9</sup> liquid crystals,<sup>10</sup> organic light-emitting diodes,<sup>11</sup> as components of various types of fluorescent polymers and dendrimers,<sup>12</sup> photoactive polypeptides,<sup>13</sup> and genetic probes.<sup>14</sup> Moreover,  $\pi$ -extended pyrene derivatives emitted significantly red-shifted fluorescence with enhanced quantum yield compared to the parent pyrene.<sup>15–20</sup> However, except for one example employing pyrene as the edge substituent,<sup>21</sup> there has been no report on the two-photon materials utilizing pyrene as the  $\pi$ -center.

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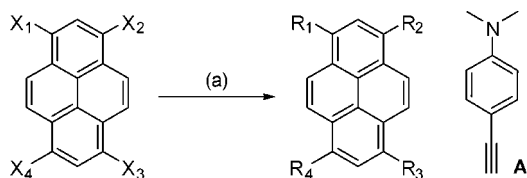
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SCHEME 1. Synthesis of 1–5<sup>a</sup>

- 6: X<sub>1</sub> = Br, X<sub>2</sub> = X<sub>3</sub> = X<sub>4</sub> = H  
 7: X<sub>1</sub> = X<sub>3</sub> = Br, X<sub>2</sub> = X<sub>4</sub> = H  
 8: X<sub>1</sub> = X<sub>4</sub> = Br, X<sub>2</sub> = X<sub>3</sub> = H  
 9: X<sub>1</sub> = X<sub>2</sub> = X<sub>3</sub> = Br, X<sub>4</sub> = H  
 10: X<sub>1</sub> = X<sub>2</sub> = X<sub>3</sub> = X<sub>4</sub> = Br
- 1: R<sub>1</sub> = A, R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H  
 2: R<sub>1</sub> = R<sub>3</sub> = A, R<sub>2</sub> = R<sub>4</sub> = H  
 3: R<sub>1</sub> = R<sub>4</sub> = A, R<sub>2</sub> = R<sub>3</sub> = H  
 4: R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = A, R<sub>4</sub> = H  
 5: R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = A

<sup>a</sup> Reagents and conditions: (a) A (1–4 equiv), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, PPh<sub>3</sub>, Et<sub>3</sub>N, THF, 70 °C, 12 h.

In this work, we have synthesized a series of pyrene derivatives having 4-(*N,N*-dimethylamino)phenylethynyl groups (1–5) as the substituent. The usefulness of pyrene as a  $\pi$ -center and the effects of increasing the number of substituents and molecular symmetry on the one- and two-photon spectroscopic properties have been studied.

Pyrene derivatives (1–5) have been synthesized by the Sonogashira coupling reaction<sup>22</sup> between bromopyrenes (6–10) and 4-ethynyl-*N,N*-dimethylaniline (A) as shown in Scheme 1. 1-Bromo- (6), a mixture of 1,6- and 1,8-dibromo- (7 and 8), 1,3,6-tribromo- (9), and 1,3,6,8-tetrabromopyrenes (10) were prepared by the bromination<sup>23</sup> of pyrene with 1 to 4 equiv of bromine. Mono-, tris-, and tetrakis[4-(*N,N*-dimethylamino)phenylethynyl]pyrene (1, 4, and 5) have been synthesized by the ethynylation reaction. To obtain 2 and 3, a mixture of 7 and 8 was reacted with A and the product mixture was separated by crystallization followed by column chromatography.

One-photon absorption spectra of 1–5 in toluene are broad and complicated due to the complexity of the molecular structure. However, a gradual bathochromic shift in the  $\lambda_{\max}$  is clearly observed in the order 1 < 2  $\approx$  3 < 4 < 5 (Figure S1 (Supporting Information) and Table 1), indicating that the extent of intramolecular charge transfer (ICT) increases with the conjugation length. The molar extinction coefficient ( $\epsilon$ ) increases sharply from 1 to 2, and remains nearly the same after further increase in the molecular size (Table 1).

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TABLE 1. Photophysical Data for 1–5

compd	$\lambda_{\max}$ (10 <sup>-4</sup> $\epsilon$ ) <sup>a</sup>	$\lambda_{\text{fl}}^b$	$\Delta\tilde{\nu}^c$	$\Phi^d$	$\lambda_{\max}^{(2)}$ <sup>e</sup>	$\delta_{\max}^f$	$\Phi\delta_{\max}^g$
1	396 (1.59)	474	4155	0.90	830	55	50
2	431 (6.69)	481	2412	1.00	760	490	490
3	430 (4.06)	483	2552	1.00	760	230	230
4	478 (6.06)	506	1158	1.00	780	530	530
5	508 (6.94)	534	958	1.00	820	1150	1150

<sup>a</sup>  $\lambda_{\max}$  of the one-photon absorption spectra in nm. The numbers in parentheses are molar extinction coefficients. <sup>b</sup>  $\lambda_{\max}$  of the one-photon fluorescence spectra in nm. <sup>c</sup> Stokes shift in cm<sup>-1</sup>. <sup>d</sup> Fluorescence quantum yield,  $\pm 10\%$ . <sup>e</sup>  $\lambda_{\max}^{(2)}$  of the two-photon absorption spectra in nm. <sup>f</sup> Two-photon absorptivity in 10<sup>-50</sup> cm<sup>4</sup> s per photon (GM),  $\pm 15\%$ . <sup>g</sup> Two-photon action cross section in GM at  $\lambda_{\max}^{(2)}$ .

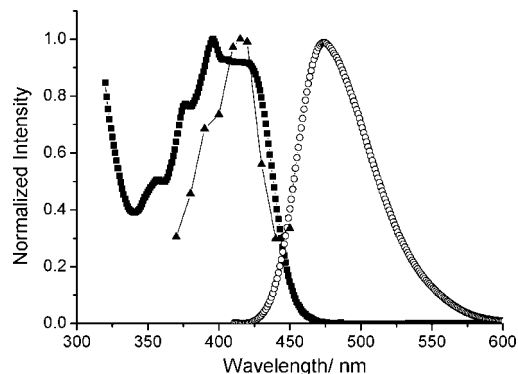


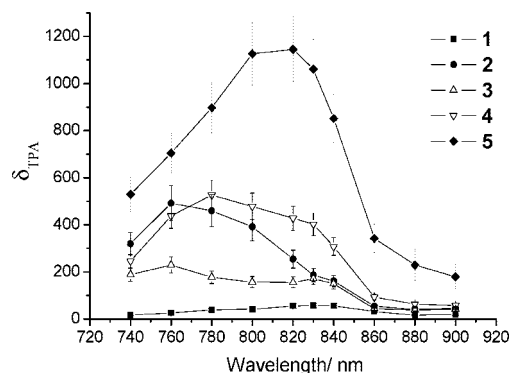
FIGURE 1. Normalized one-photon absorption (■), emission (○), excitation at  $\lambda_{\max}$ , and two-photon excitation spectra (▲) for 1 in toluene. The two-photon spectrum is plotted against  $\lambda/2$  (twice the photon energy).

The fluorescence spectra of 1–5 exhibit a single peak (Figure S1, Supporting Information), which indicates that the emission occurs from the lowest excited state with the largest oscillator strength. The emission spectra show systematic bathochromic shifts with the conjugation length increase, that is, 1 < 2  $\approx$  3 < 4 < 5, implying that the energy gap between ground and excited states decreases in this order (Table 1). The fluorescence Stokes shift decreases in the order 1 > 2  $\approx$  3 > 4 > 5 (Table 1); the energy gap between the Franck–Condon and emitting states decreases in the same order. This is presumably because the ICT is more similar between the ground and excited states of the extended molecules. A similar result was reported for 9,10-bis(arylethynyl)anthracene derivatives.<sup>24</sup> All compounds are strongly fluorescent with high fluorescence quantum yields.

The two-photon cross section was measured by the two-photon-induced fluorescence measurement technique, using the femtosecond laser pulses as described.<sup>4c</sup> In all cases, the output intensity of two-photon excited fluorescence (TPEF) was linearly dependent on the square of the input laser intensity, thereby confirming the nonlinear absorption (Figure S3, Supporting Information).

For compounds 1, 3, and 4, one- and two-photon spectra overlap reasonably well in terms of the total absorption energy (Figures 1 and S4 (Supporting Information)). This indicates that the two-photon allowed states of the dipoles are close to the one-photon allowed states, as predicted by symmetry. On the other hand, the  $\lambda_{\max}^{(2)}/2$  of 2 is located at a shorter wavelength than  $\lambda_{\max}$ . This is again consistent with the prediction that the two-photon allowed states for the quadrupoles should be located

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**FIGURE 2.** Two-photon excitation spectra of **1–5** in toluene. The values are an average of three measurements.

at a higher energy than that of the one-photon allowed states.<sup>25</sup> An exception to this trend is the reasonable overlap between the one- and two-photon spectra of **5**. Although the origin of this dichotomy is not clear, perhaps this might be the reason for the larger  $\delta_{\max}$  value of **5** than others (vide infra).

All compounds show modest to large two-photon cross sections ranging from 55 to 1150 GM at 780–830 nm (Figure 2). The  $\delta_{\max}$  value increased by approximately 9-fold as the conjugation length was increased from **1** to **2**. The value of  $\delta_{\max} = 490$  GM for **2** is similar to  $\delta_{\max} = 540$  GM reported for 9,10-bis[4-(*N,N*-didecylamino)phenylethynyl]anthracene.<sup>24</sup> Moreover, the two-photon action cross section of **2** ( $\Phi\delta_{\max} = 490$  GM) is significantly larger than  $\Phi\delta_{\max} = 290$  GM for the latter due to the larger fluorescence quantum yield, which is of particular advantage in applications that use TPEF. This result implies that pyrene is as efficient a  $\pi$ -center as anthracene in two-photon materials. Interestingly, the  $\delta_{\max}$  value of **3** is nearly half that of **2**. A similar result was reported for 2,6-bis(*p*-dihexylaminostyryl)anthracene ( $\delta = 1100$  GM) whose  $\delta$  value decreased significantly in the 2,7-isomer ( $\delta_{\max} = 720$  GM).<sup>4f</sup> Hence, the linear molecules seem to have a certain advantage in enhancing the two-photon cross section. When the molecular size was increased to **4**, the  $\delta$  value increased slightly. However, a further increase in the molecular size from **4** to **5** enhanced the  $\delta_{\max}$  value by more than 2-fold despite a modest increase in MW. Moreover, the  $\Phi\delta_{\max}$  value of **5** is comparable to that of the most efficient two-photon materials<sup>4f</sup> due to the significant two-photon cross section and large fluorescence quantum yield. Furthermore, the  $\delta_{\max}$  values of quadrupolar molecules (**2**, **5**) are always larger than those of dipolar molecules (**1**, **3**, **4**) having comparable MW. This result underlines the importance of molecular symmetry consideration in the design of efficient two-photon materials.

In conclusion, we have synthesized a series of [4-(*N,N*-dimethylamino)phenylethynyl]pyrene derivatives (**1–5**). Comparison of the  $\delta_{\max}$  values with related compounds reveals that pyrene is an efficient  $\pi$ -center similar to anthracene as two-photon absorbable materials. The  $\delta_{\max}$  value of compounds increased with the number of substituents reaching the maximum value of 1150 GM for **5**. Moreover, the  $\Phi\delta_{\max}$  value of **5** is comparable to that of the most efficient two-photon materials. To the best of our knowledge, this is the first example of two-photon materials bearing pyrene as the  $\pi$ -center, and will provide a useful guideline to the design of TPA molecules.

## Experimental Section

**General Procedure for Alkyne Coupling.** Bromopyrenes were synthesized by bromination of pyrene.<sup>23</sup> The bromopyrenes [**1**- (**6**), 1,6-di- (**7**), 1,8-di- (**8**), 1,3,6-tri- (**9**), and 1,3,6,9-tetra- (**10**)] were coupled with 4-ethynyl-*N,N*-dimethylaniline under Sonogashira conditions to give compounds **1–5**.

**1-[4-(*N,N*-Dimethylamino)phenylethynyl]pyrene (1).** 1-Bromopyrene (100 mg, 0.36 mmol), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (25 mg, 0.030 mmol), CuI (7.0 mg, 0.030 mmol), PPh<sub>3</sub> (9.0 mg, 0.030 mmol), and 4-ethynyl-*N,N*-dimethylaniline (72 mg, 0.50 mmol) were added to a degassed solution of Et<sub>3</sub>N (20 mL) and THF (20 mL) under N<sub>2</sub>. After the mixture was stirred at 70 °C for 12 h, the product was poured into CH<sub>2</sub>Cl<sub>2</sub> (200 mL) and water (200 mL). The organic layer was separated and dried over anhydrous MgSO<sub>4</sub>, then the solvent was removed in vacuo. Column chromatography using silica gel with hexane:ethyl acetate (3:1) gave 78 mg (63%) of yellow solid. Mp 169 °C. IR (KBr pellet, cm<sup>-1</sup>) 2915, 2845, 2195 (C≡C), 1592, 1520, 1345 (C–N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.69 (d, *J* = 9.1 Hz, 2 H), 8.22–7.99 (m, 8 H), 7.62 (d, *J* = 9.1 Hz, 2 H), 6.74 (d, *J* = 9.1 Hz, 2 H), 3.03 (s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.4, 133.1, 131.7, 131.5, 131.4, 130.8, 129.5, 128.2, 127.9, 127.6, 126.3, 126.1, 125.6, 125.5, 124.8, 124.6, 119.2, 112.2, 96.9, 86.9, 40.5. FAB MS *m/z* (M<sup>+</sup>) calcd 345.42, found 345.23. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.58; H, 5.21; N, 4.19.

**1,6-Bis[4-(*N,N*-dimethylamino)phenylethynyl]pyrene (2) and 1,8-Bis[4-(*N,N*-dimethylamino)phenylethynyl]pyrene (3).** A mixture of **7** and **8** (200 mg, 0.55 mmol), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (19 mg, 0.028 mmol), CuI (10 mg, 0.050 mmol), PPh<sub>3</sub> (14 mg, 0.050 mmol), and 4-ethynyl-*N,N*-dimethylaniline (190 mg, 1.4 mmol) was added to a degassed solution of Et<sub>3</sub>N (20 mL) and THF (20 mL) under N<sub>2</sub>. After stirring at 70 °C for 12 h, the reaction mixture was poured into CH<sub>2</sub>Cl<sub>2</sub> (200 mL) and water (200 mL). The organic layer was separated and dried over anhydrous MgSO<sub>4</sub> and the solvent was removed in vacuo. A 50 mL solution of hexane:ethyl acetate (4:1) was added and yellow solid was precipitated from the solution. Filtration of the solid gave 53 mg (19%) of **2** in a yellow solid. The filtrate was evaporated in vacuo and the crude product was then subjected to column chromatography (silica gel) with hexane:ethyl acetate (3:7) to give 40 mg (15%) of **3** in a yellow solid.

Compound **2**: Mp >300 °C dec. IR (KBr pellet, cm<sup>-1</sup>) 2917, 2850, 2194 (C≡C), 1596, 1523, 1350 (C–N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.66 (d, *J* = 8.81 Hz, 2 H), 8.10–8.18 (m, 6 H), 7.58 (d, *J* = 9.05 Hz, 4 H), 6.73 (d, *J* = 9.05 Hz, 4 H), 3.30 (s, 12 H). <sup>13</sup>C NMR could not be determined due to its low solubility. FAB MS *m/z* (M<sup>+</sup>) calcd 488.62, found 488.27. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>: C, 88.49; H, 5.78; N, 5.73. Found: C, 88.28; H, 5.71; N, 5.59.

Compound **3**: Mp 198 °C. IR (KBr pellet, cm<sup>-1</sup>) 2915, 2852, 2192 (C≡C), 1591, 1527, 1357 (C–N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.77 (s, 2 H), 8.18–8.08 (m, 4 H), 8.02 (s, 2 H), 7.06 (d, *J* = 9.02 Hz, 4 H), 6.74 (d, *J* = 9.02 Hz, 4 H), 3.04 (s, 12 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.4, 133.1, 131.7, 131.0, 129.7, 127.7, 126.6, 125.1, 124.6, 119.5, 112.1, 110.4, 97.2, 87.0, 40.5. FAB MS *m/z* (M<sup>+</sup>) calcd 488.62, found 488.30. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>: C, 88.49; H, 5.78; N, 5.73. Found: C, 88.61; H, 5.55; N, 5.81.

**1,3,6-Tris[4-(*N,N*-dimethylamino)phenylethynyl]pyrene (4).** 1,3,6-Tribromopyrene (100 mg, 0.23 mmol) and 4-ethynyl-*N,N*-dimethylaniline (116 mg, 0.79 mmol) were used and the reaction was carried out by the same method as that for **1**. Column chromatography using silica gel with hexane:ethyl acetate (1:1) gave 103 mg (71%) of orange-red solid. Mp 210 °C. IR (KBr pellet, cm<sup>-1</sup>) 2185 (C≡C), 1594, 1527, 1359 (C–N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.75 (s, 2 H), 8.64 (d, *J* = 9.00 Hz, 1 H), 8.37 (s, 1 H), 8.18–8.08 (m, 3 H), 7.60 (d, *J* = 9.00 Hz, 6 H), 6.74 (d, *J* = 9.00 Hz, 6 H), 3.04 (s, 18 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  150.4, 135.1, 134.9, 133.1, 132.4, 132.3, 132.2, 131.3, 131.1, 128.8, 128.6, 124.7, 124.7, 124.5, 119.8, 119.3, 112.1, 110.4, 110.3, 97.51, 97.25,

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97.1, 87.1, 86.5, 86.48, 40.4. FAB MS  $m/z$  ( $M^+$ ) calcd 631.81, found 631.00. Anal. Calcd for  $C_{21}H_{21}N_3O_2$ : C, 87.45; H, 5.90; N, 6.65. Found: C, 87.33; H, 5.98; N, 6.49.

**1,3,6,8-Tetrakis[4-(*N,N*-dimethylamino)phenylethynyl]pyrene (5).** 1,3,6,9-Tetrabromopyrene (100 mg, 0.19 mmol) and 4-ethynyl-*N,N*-dimethylaniline (126 mg, 0.85 mmol) were used. Column chromatography on silica gel with hexane:CH<sub>2</sub>Cl<sub>2</sub> (1:4) provided 58 mg (40%) of **5** in a red solid. Mp <300 °C dec. IR (KBr pellet, cm<sup>-1</sup>) 2190 (C≡C), 1608, 1523, 1361. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.72 (s, 4 H), 8.35 (s, 2 H), 7.60 (d,  $J = 9.00$  Hz, 8 H), 6.74 (d,  $J = 9.00$  Hz, 8 H), 3.04 (s, 24 H). <sup>13</sup>C NMR of this compound cannot be determined due to its low solubility. FAB MS  $m/z$  ( $M^+$ ) calcd 774.99, found 774.00. Anal. Calcd for  $C_{21}H_{21}N_3O_2$ : C, 86.79; H, 5.98; N, 7.23. Found: C, 86.92; H, 6.01; N, 7.35.

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**Supporting Information Available:** General methods, solubility test, measurement of two-photon cross section, and UV/vis, fluorescence, and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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