

Ph₂N-Substituted Ethylene-Bridged *p*-Phenylene Oligomers: Synthesis and Photophysical and Redox Properties

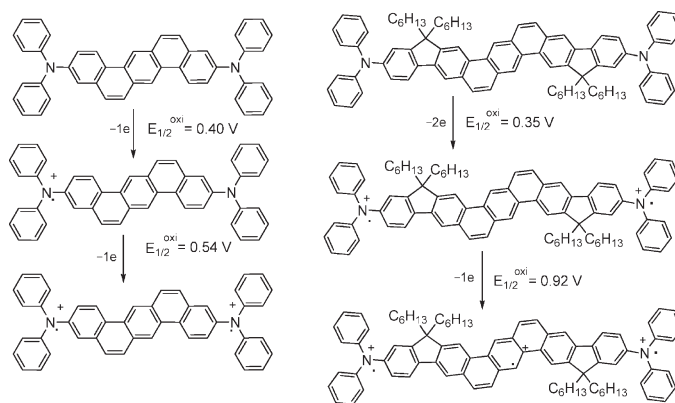
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Received October 14, 2010



For a series of *p*-phenylene-based oligomers terminated with two triphenylamines, their absorption, photoluminescence, and band gaps show a pattern of extensive π -conjugation with increasing array size. Oligomers with large central arrays have greater quantum yields than their small analogues. Cyclic voltammetric (CV) measurements indicated two-step oxidations of the two diphenylamino groups for compounds **1–5** and one-step oxidations for the two amines of large oligomers **6** and **7**.

Introductions

p-Phenylene-based oligomers have diverse applications in optoelectronic applications including organic light-emitting diodes (OLED),¹ field-effect transistors,² and photovoltaic devices.³ Scheme 1 shows representative classes of *p*-phenylene oligomers bearing repeated units including *p*-phenylene (A),⁴

fluorene (B),⁵ tetrahydropyrene (C),⁶ and ladder-typed phenylene (D).⁷ For these oligomers, each repeated unit is linked by a σ C–C bond, which impedes the π -electron delocalization by the nonplanarity of benzene arrays.

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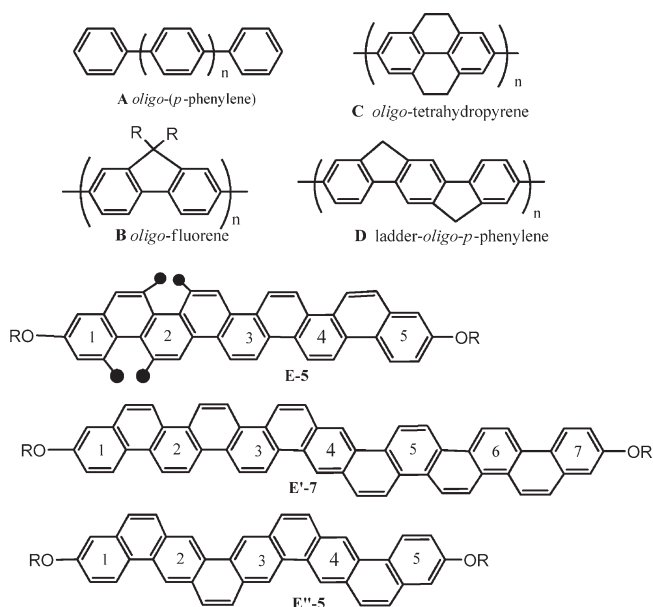
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SCHEME 1



We reported⁸ the stereocontrolled synthesis of ethene-bridged *p*-phenylenes of three series, denoted **E**, **E'**, and **E''** as depicted in Scheme 1. These oligomers fail to show efficient electron-delocalization, and a moderate energy gap of 2.75 eV was obtained for the seven-benzene array **E'-7**. Variable-temperature NMR spectra revealed⁸ small energy barriers for the distortion of planarity of the large benzene arrays.⁹ We propose that steric interactions of their “bay” hydrogen pairs are the primary factor of such a distortion.

Triarylamines are useful materials as the host layer in OLED devices because they accelerate the transport of holes.^{10,11} Aromatic hydrocarbons bearing triarylamines serve as dopants in OLED devices because of their high quantum yields and decreased energy gaps. A *p*-phenylene-

based array terminated with two triarylamines is an idealized model to test the degree of charge delocalization through sequential oxidations of two triarylamines.^{12,13} In this work, we prepared new ethene-bridged *p*-phenylenes **1–7** terminated with two triphenylamines to examine their photophysical and redox properties (Scheme 2). Compounds **1**, **3**, **4**, and **7** are the standard forms of ethene-bridged *p*-phenylenes with spacers of varied lengths. We also prepared compound **2** that serves as an intermediate between **1** and **3**. Compounds **5** and **6** are related to oligomer **4** with the replacement of the two terminal benzenes with naphthalenes and fluorenes.

Results and Discussion

Schemes 3–4,5,6,7,8,9 show the synthetic protocols for compounds **1–7** with platinum- and ruthenium catalyzed aromatizations of 1-alkynyl-2-arylbenzenes. We used these two catalytic reactions for the stereocontrolled synthesis of ethene-bridged *p*-phenylenes.⁸ In the platinum catalysis, an addition of the 2-naphthyl or phenanthryl group to the adjacent internal alkyne occurs at the more hindered carbon, as exemplified by species **2d**, **3a**, and **5c**. An opposite regioselectivity was observed for ruthenium catalysis in that the less hindered aryl carbon is the preferable site for addition to the terminal alkyne,⁸ as shown by species **6b**. Preparation of compound **1** relies on the initial coupling of borate **1a** and **1b**, giving the resulting product **1c** in 92% yield. Treatment of **1c** with $\text{TpRuPPh}_3(\text{CH}_3\text{CN})_2\text{SbF}_6$ (10 mol %) in hot DCE (80 °C, 12 h) delivered phenanthrene species **1d** that was subsequently converted to **1e** through sequential treatment with BBr_3 and Tf_2O /pyridine. A final Buchwald coupling¹⁴ of triflate derivative **1e** with diphenylamine gave desired compound **1** in 61% yield. Toward the synthesis of compound **2**, we performed two Pd-catalyzed coupling reactions of initial **2a** to obtain key intermediate **2d**. A subsequent PtCl_2 -catalyzed aromatization of species **2d** gave compound **2e** that was ultimately transformed into desired **2** following repeated procedures. Such a platinum catalysis served again for the stereocontrolled synthesis of compound **3** through the aromatization of key species **3a**, which was readily obtained from the Suzuki-coupling¹⁵ of phenanthryl triflate **1e** with borate **2c**. We designed also a 2-fold aromatization of species **4b** to obtain a distinct oligomer **4**, as depicted in Scheme 6. Similar *p*-phenylene oligomers **5** and **7** were synthesized smoothly with platinum-catalyzed 2-fold aromatization of key species **5c** and **7b**, as depicted in Schemes 7 and 9. Such a 2-fold aromatization is also applicable to the stereoselective synthesis of a large oligomer **6**; the protocol is shown in Scheme 8. Compounds **1–7** are stable in air and fully characterized with ¹H and ¹³C NMR, MALDI, or high-resolution mass and elemental analysis.

Figures 1 and 2 show the UV and PL spectra of compounds **1–7**, and their corresponding photophysical properties are summarized in Table 1. In Figure 1 (left), the absorption spectra indicate compounds **1**, **2**, **3**, and **7** have similar patterns in several electronic absorptions whereas species **4** belongs to a

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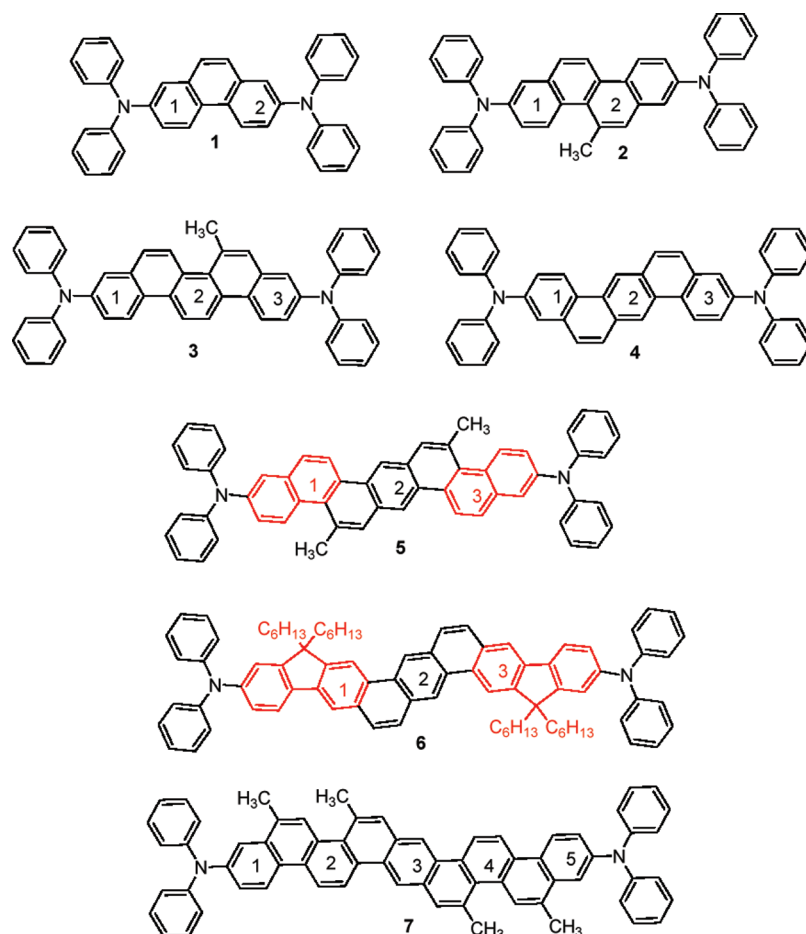
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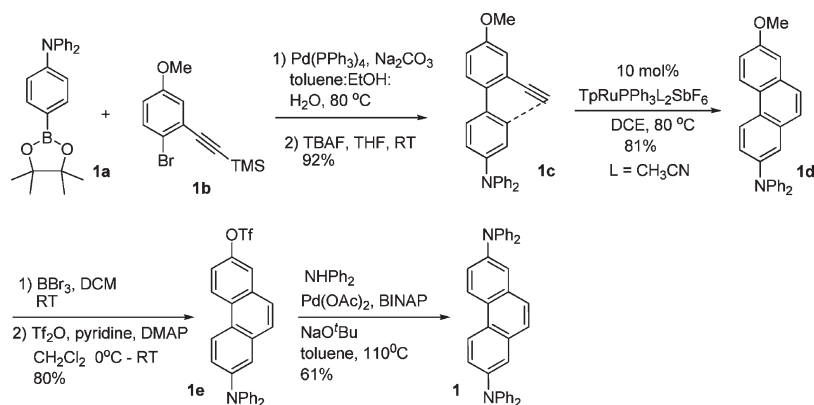
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SCHEME 2



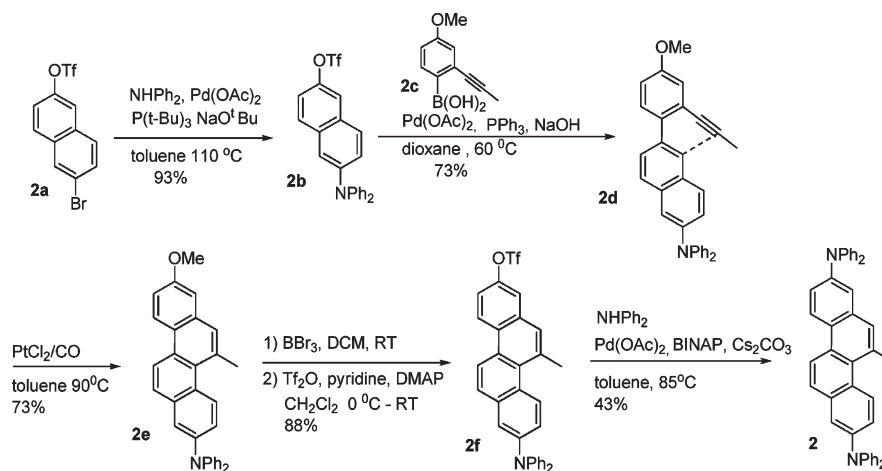
SCHEME 3



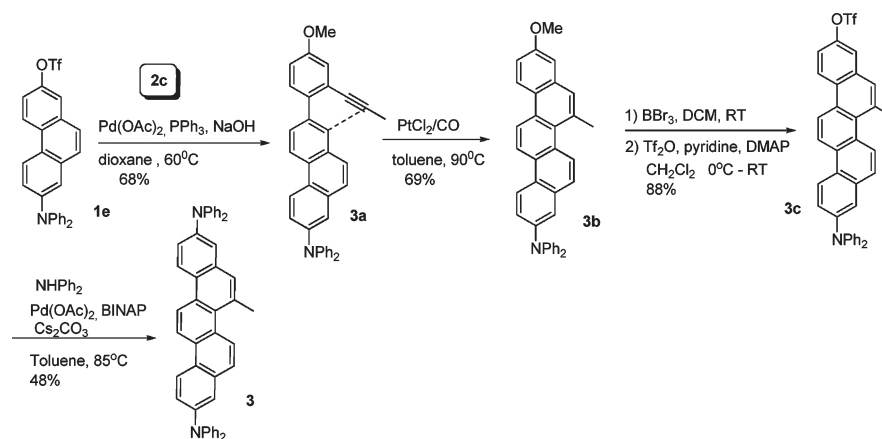
distinct family due to its different absorption pattern. For the former family, the absorption maxima at the 360–400 nm regions gradually move to long wavelengths with increasing benzene arrays. We observed three absorption bands for compounds **4**, **5**, and **6**, but their intensity patterns are different from each other. Notably, compound **6** bearing a 9-diphenylaminofluorenyl group has a strong absorption at the low electronic states. The observed wavelengths of this low electronic state follow the lengths of their benzene arrays: **4** (388 nm) < **5** (394 nm) < **6** (410 nm).

Figure 2 (left) shows the fluorescent emission of compounds **1**, **2**, **3**, **4**, and **7**; their wavelengths reflect the extensive conjugation, with 434 nm for species **1** and 471 nm for species **7**. Figure 2 (right) shows the emission spectra of the remaining species, of which the emission wavelengths follow the order **5** (470 nm) > **6** (458 nm) > **4** (451 nm). Diamines **1–7** were strongly fluorescent in CH_2Cl_2 ($1 \times 10^{-5} \text{ M}$); their quantum yields in Table 1 were measured carefully and reproducibly. For small arrays **1–3**, their quantum yields were similar to the 24.2–26.9% in CH_2Cl_2 , but

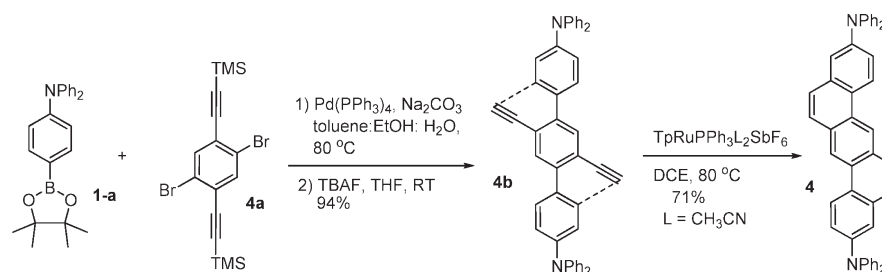
SCHEME 4



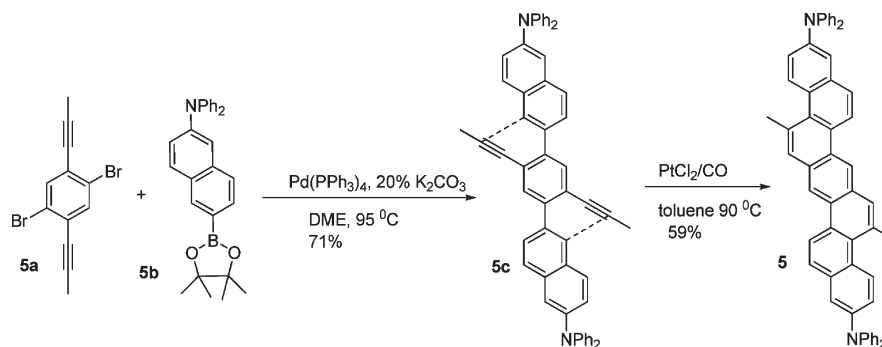
SCHEME 5



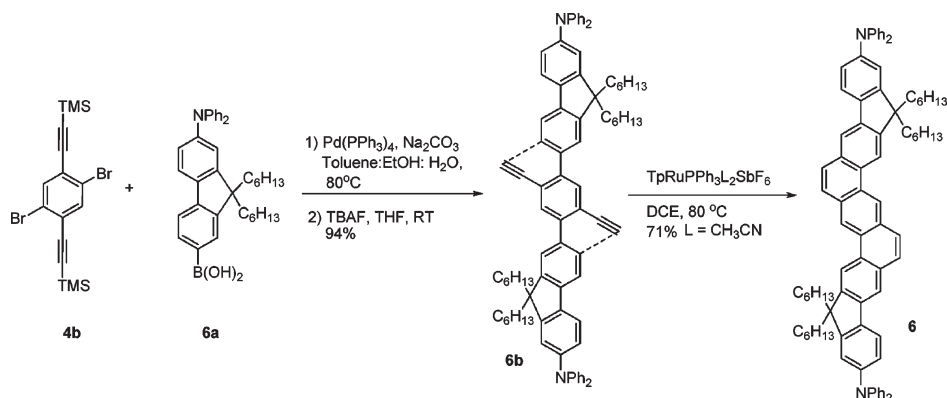
SCHEME 6



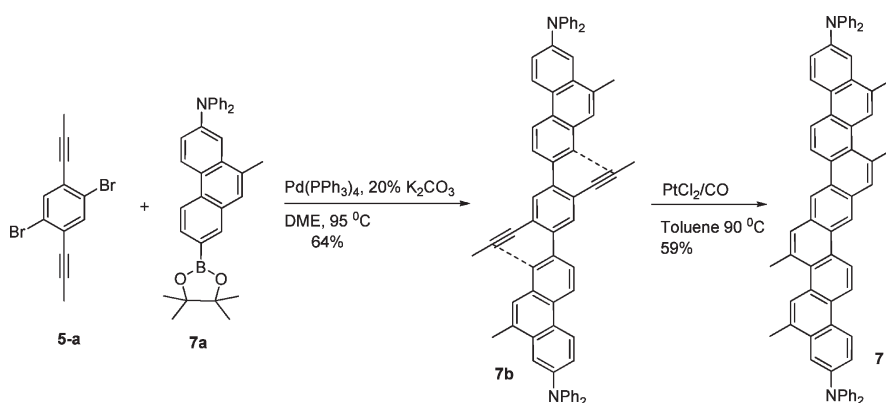
SCHEME 7



SCHEME 8



SCHEME 9



increased rapidly to 47.2%, 56.6%, and 56.2% for species **4**, **5**, and **7**, and up to 96.3% for diamine **6**. At a dense concentration (10^{-4} M), all of these diamine compounds **1–7** showed decreased quantum yields, presumably due to a high extent of molecular aggregations; their absorption and emission spectra remained unchanged under such conditions. We compared the charge transfer properties for representative species **2**, **4**, **5**, and **6** on measuring their PL spectra in toluene and CH_2Cl_2 . The emission maxima of **2**, **4**, **5**, and **6** in toluene appeared at 429, 439, 443, and 449 nm, respectively. Relative to those maxima in CH_2Cl_2 , we observed the magnitude of red-shifts 12, 13, 27, and 9

nm for **2**, **4**, **5**, and **6**, respectively. Accordingly, charge transfer properties are not the primary factor to rationalize the large quantum yields of oligomers **4–7**.

As a transition to the lowest electronic state (S_1) is forbidden by symmetry for compounds **1–7**, most of them are not recognizable.⁸ We determined the optical gaps, listed in Table 1, from the intersection of the absorption and fluorescence spectrum. Compound **1** has a band gap of ca. 3.10 eV that gradually decreases to 3.04 eV for compound **2**, 2.96 eV for species **3**, and 2.89 eV for **7**. The small decrease in energy gap, as shown by the five-benzene array **7**, is not surprising because its benzene array is easily twisted from

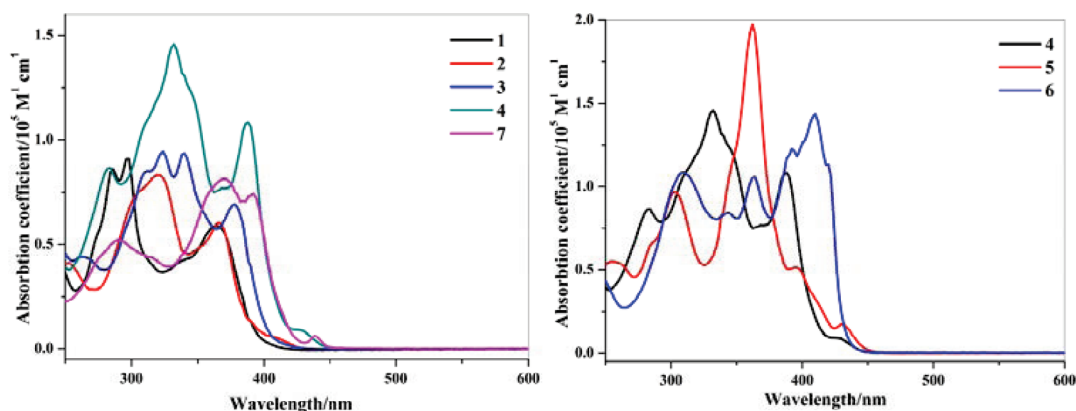


FIGURE 1. Absorption spectra of compounds **1–4** and **7** (left) and **4–6** (right) in CH_2Cl_2 (1×10^{-5} M).

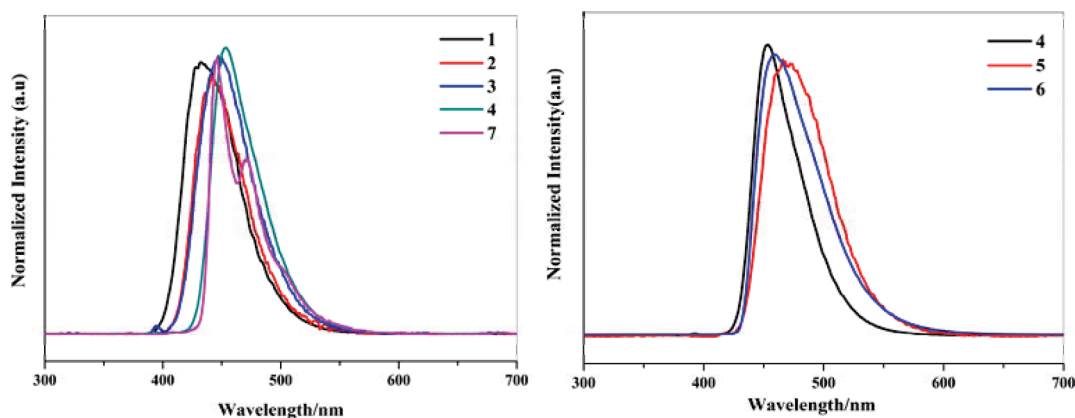


FIGURE 2. Emission spectra of compounds 1–4 and 7 (left) and 4–6 (right) in CH_2Cl_2 (1×10^{-5} M).

TABLE 1. Photophysical Properties of Compounds 1–7

compd	Abs _{max} ^a (nm)	PL _{max} ^a (nm)	Q.Y. ^{a,b} (%)	HOMO/LUMO ^d (eV)	band gap ^c (eV)
1	286, 298, 364	434	24.2 (21.8) ^c	5.07/1.97	3.10
2	320, 366	441	26.2 (23.2)	5.17/2.13	3.04
3	324, 340, 378	446	26.9 (24.1)	5.22/2.26	2.96
4	284, 332, 388	451	47.2 (41.9)	5.20/2.28	2.92
5	302, 364, 394	470	56.6 (51.8)	5.21/2.45	2.76
6	310, 364, 410	458	96.3 (93.5)	5.15/2.33	2.82
7	290, 370, 392	446, 471	56.2 (51.5)	5.24/2.35	2.89

^aIn CH_2Cl_2 , 1×10^{-5} M. ^bCoumarin I as a standard. ^cThe data in parentheses correspond to 10^{-4} M. ^dThe energy levels of HOMO were determined from CV. ^eBand gaps were calculated from UV absorption.

TABLE 2. Oxidation/Reduction Potentials of Compounds 1–7

compd	1st $E_{1/2}^{\text{oxi}}$ ^a	2nd $E_{1/2}^{\text{oxi}}$ ^a	$E_{1/2}^{\text{red}}$ ^b
1	0.27	0.58	
2	0.37	0.60	
3	0.42	0.56	−1.37
4	0.40	0.54	−1.41
5	0.41	0.51	−1.35
6	0.35	0.92	−1.35
7	0.44		

^aMeasured in CH_2Cl_2 . ^bMeasured in DMF.

planarity.⁸ Notably, regioisomers **3** and **4** have comparable values 2.96–2.92 eV. For the three-benzene arrays, compound **5** has a band gap of 2.76 eV, smaller than those of **4** (2.92 eV) and of **6** (2.82 eV). Compounds **1–7** show one- or two-step reversible oxidations in CH_2Cl_2 according to cyclic voltammetry measurements. We estimated their HOMO–LUMO gaps from their oxidation potential and band gaps, as depicted in Table 1.

The electrochemical properties of ethylene-bridged *p*-phenylenes (PAHs) **1–7** terminated with two amines were probed by cyclic voltammetry (CV) (Table 2). All reduction and oxidation potentials recorded here are relative to the redox couple of ferrocene/ferrocenium (Fc/Fc^+). The oxidation CV were measured in CH_2Cl_2 , whereas reduction CV were conducted in DMF. Most compounds tested here exhibited two reversible oxidation potentials and one reversible reduction feature (Figures 3 and 4). Among these compounds, molecule **1** exhibited the smallest oxidation potentials (0.27 V), compared to those of compounds **2–5** that showed their first oxidation potentials at about 0.40 V. The second oxidation potentials of **1–5** are around 0.5–0.6 V. For species **1–5**, we assign the first and second oxidations to the removal of the first and second electrons of the two amine

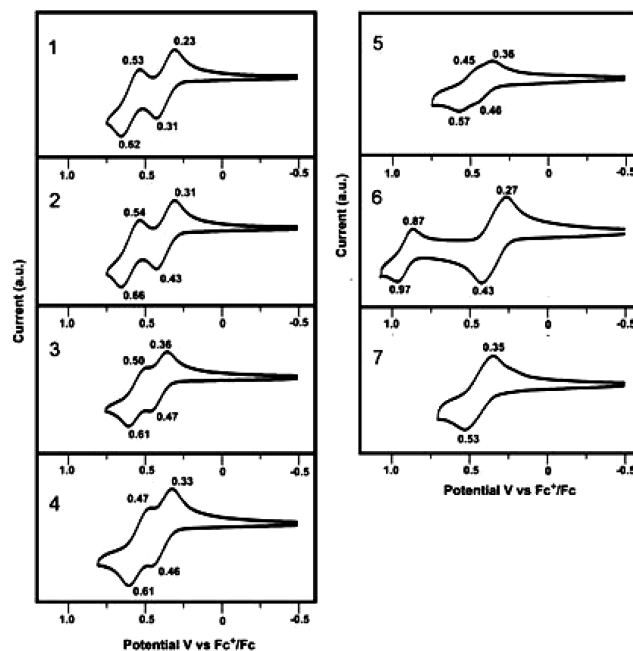


FIGURE 3. Oxidation CV of compounds 1–7 in CH_2Cl_2 .

groups. For compound **1**, the triphenylamine renders the other amine readily oxidizable because of a small phenanthrene spacer; this hypothesis rationalizes the first oxidation potential of species **1** at 0.27 V. Once the amine radical cation is formed, the other amine becomes more difficult to oxidize for a small spacer. This assessment is demonstrated by a large difference, 0.31 V, between the two oxidation potentials, 0.27 and 0.58 V, for species **1**; the difference became small with

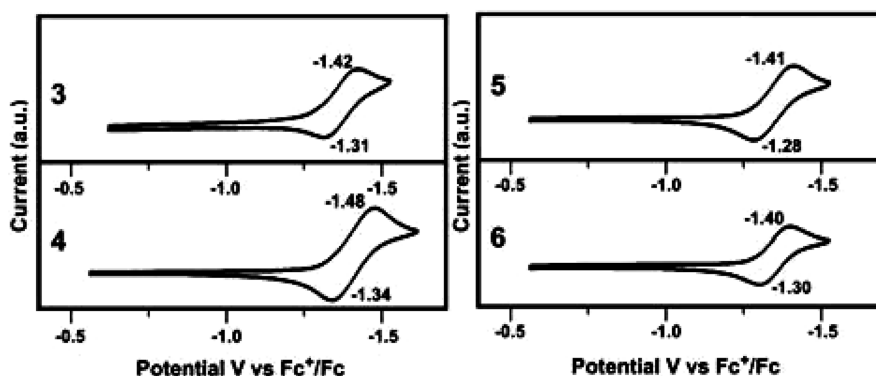


FIGURE 4. Reduction CV of compounds 3–6 in DMF.

increasing size of the spacer as in species **3** (0.14 V), **4** (0.14 V), and **5** (0.10 V). The lack of reduction potentials of species **1** and **2** reflects their electron-rich phenanthrene and chrysene spacers donated by two amines. Regioisomers **3** and **4** have nearly identical oxidation and reduction potentials. For species **6**, we assign the first oxidation potential, 0.35 V, to simultaneous oxidations of two amines at one stage, which behave like two independent groups because of a large spacer. The second oxidation at the high potential (0.92 V) of species **6** is attributed to formation of a trication species through the oxidation of the central core. For the largest oligomer **7**, we observed a single-step oxidation, at 0.44 V, of the two amines at 0.44 V, without formation of a trication species, likely because of its poor solubility in CH_3CN (5×10^{-4} M); this low solubility accounts also for the absence of reduction potentials in DMF.

Conclusions

In summary, we prepared a series of *p*-phenylene-based oligomers terminated with two triphenylamines. The absorption spectra, photoluminescence, and band gaps of these oligomers show a pattern of extensive π -conjugation with increasing array sizes. We observed fluorescent behaviors such that large arrays have greater quantum yields than their small analogues; this phenomenon is attributed to the easy distortion from planarity of large arrays. Cyclic voltammetric (CV) measurements indicated two-step oxidations of the two amino groups for compounds **1**–**5**; the two potentials approach each other with increasing sizes of spacer. The two amines of large arrays **6** and **7** show one-step oxidation, implying that the large spacers impede an extensive delocalization of cation charge.

Experimental Section

1. Experimental Procedures for the Synthesis of Oligomer 1. a. Synthesis of 2'-Ethynyl-4'-methoxy-*N,N*-diphenylbiphenyl-4-amine (1c). A solution of toluene (80 mL), ethanol (20 mL), and water (20 mL) was degassed for over 30 min, and to this solution was added compound **1b**⁸ (2.00 g, 7.48 mmol), Pd(PPh₃)₄ (864 mg, 0.748 mmol), Na₂CO₃ (7.9 g 74.84 mmol), and borate **1a**⁸ (3.33 g, 8.98 mmol). The mixture was stirred at 80 °C for 12 h. The solution was cooled to room temperature and quenched with water; the organic layer was extracted with CH₂Cl₂, dried over MgSO₄, and concentrated under reduced pressure. The crude product was eluted through a silica column

(EA:hexane = 5:95) to afford coupling product (2.54 g, 76%) as a yellow oil. To a solution of this silyl compound (1.8 g, 4.02 mmol) in THF (20 mL) was added *n*-tetrabutylammonium fluoride (1.0 M in THF, 6.03 mL, 6.03 mmol) at 0 °C, and the resulting mixture was stirred at 0 °C for 2 h. Column chromatography of the crude material on silica gel (EA/hexane = 5:95) afforded compound **1c** (1.38 g, 92%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.4 Hz, 2 H), 7.34–7.27 (m, 5 H), 7.19–7.12 (m, 7 H), 7.05 (t, J = 7.2 Hz, 2 H), 6.99–6.96 (m, 1 H), 3.85 (s, 3 H), 3.1 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 157.9, 147.6 (2 \times C), 146.8, 133.7, 130.5, 129.8 (2 \times CH), 129.2 (4 \times CH), 124.5 (4 \times CH), 122.8 (2 \times CH), 122.7 (2 \times CH), 120.8, 118.2, 115.8, 83.3, 79.9, 55.4; HRMS calcd for C₂₇H₂₁NO 375.1623, found 375.1629.

b. Synthesis of 7-Methoxy-*N,N*-diphenylphenanthren-2-amine (1d). A flask containing TpRuPPh₃(CH₃CN)₂SbF₆ (71.4 mg, 0.08 mmol) was dried in vacuo for 2 h before it was charged with compound **1c** (300 mg, 0.79 mmol) and 1,2-dichloroethane (70 mL). The mixture was heated at 80 °C for 24 h before cooling to room temperature. After removal of the solvent in vacuo, the crude material was purified by flash column chromatography on silica gel (CH₂Cl₂:hexane = 1:20) to afford compound **1d** (243 mg, 81%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.47–8.42 (m, 2 H), 7.58 (d, J = 8.8 Hz, 1 H), 7.50–7.48 (m, 2 H), 7.39 (dd, J = 2, 6.8 Hz, 1 H), 7.29–7.20 (m, 6 H), 7.15 (d, J = 7.6 Hz, 4 H), 7.06–7.02 (m, 2 H), 3.95 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 147.8 (2 \times C), 145.4, 132.7, 132.1, 129.3 (4 \times CH), 127.0, 126.8, 126.2, 124.7, 124.2 (4 \times CH), 123.9, 123.2, 122.8 (2 \times CH), 121.8, 117.2, 108.5, 55.4; HRMS calcd for C₂₇H₂₁NO 375.1623, found 375.1615.

c. Synthesis of 7-(Diphenylamino)phenanthren-2-yltrifluoromethanesulfonate (1e). To a solution of **1d** (200 mg 0.53 mmol) in CH₂Cl₂ was added BBr₃ (160 mg, 0.64 mmol) dropwise at 0 °C, then the resulting mixture was stirred for 2 h. After quenching with saturated K₂CO₃ solution, the organic layer was extracted with dry CH₂Cl₂, dried over MgSO₄, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (CH₂Cl₂:hexane = 1:6) to afford 7-(diphenylamino)phenanthren-2-ol (175 mg, 91%) as a yellow solid. 7-(Diphenylamino)phenanthren-2-ol (300 mg, 0.83 mmol) and DMAP (10.1 mg, 0.08 mmol) were dissolved in dry CH₂Cl₂ (25 mL) at room temperature, and to this mixture was added pyridine (328 mg, 4.15 mmol) and then trifluoromethanesulfonic anhydride (351 mg, 1.25 mmol). The mixture was stirred for 2 h at room temperature before it was quenched with water. The organic layer was extracted with CH₂Cl₂, washed with diluted HCl and brine, and dried over MgSO₄. Rotary evaporation of the solvent gave a brown residue that was purified by flash column chromatography on silica gel (EA:hexane = 1:20) to afford compound **1e** (1.29 g, 87%) as a yellow

oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (d, $J = 8.8$ Hz, 1 H), 8.44 (d, $J = 8.8$ Hz, 1 H), 7.71 (d, $J = 2.4$ Hz, 1 H), 7.62–7.55 (m, 2 H), 7.48–7.43 (m, 3 H), 7.32–7.28 (m, 4 H), 7.17 (d, $J = 7.6$ Hz, 4 H), 7.10–7.07 (m, 2 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.4 (2 \times C), 147.1, 147.0, 133.4, 131.9, 129.8, 129.4 (4 \times CH), 128.5, 126.3, 124.8, 124.6 (4 \times CH) 124.5, 123.8, 123.7 (2 \times CH), 123.5, 120.2, 119.9, 119.5 (one carbon merged to others); HRMS calcd for $\text{C}_{27}\text{H}_{18}\text{F}_3\text{NO}_3\text{S}$ 493.0959, found 493.0965.

d. Synthesis of Oligomer 1. A flask was charged with NaO^tBu (58 mg, 0.60 mmol), $\text{Pd}(\text{OAc})_2$ (4.9 mg, 0.02 mmol), and BINAP (18.8 mg, 0.03 mmol), then to this solution was added a toluene (5 mL) solution of compound **1e** (200 mg, 0.40 mmol) and diphenylamine (102 mg, 0.60 mmol). The resulting mixture was stirred under argon at room temperature for 30 min before it was heated to 110 $^\circ\text{C}$ to stir for 32 h. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL), and filtered through a Celite pad. Concentration and flash

chromatography on silica gel (CH_2Cl_2 :hexane = 2:30) afforded compound **1** (126 mg, 61%) as a yellow solid. Mp 306.9–308.9 $^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.39 (d, $J = 8.7$ Hz, 1 H), 7.41(s, 1H), 7.28–7.24 (m, 5 H), 7.14–7.12 (m, 4 H), 7.05–7.01 (m, 2 H); $^{13}\text{C NMR}$ (150 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) δ 147.8 (2 \times C), 145.9, 132.7, 129.4 (4 \times CH), 126.9, 126.0, 124.4 (4 \times CH), 123.5, 123.1 (2 \times CH), 121.2, 118.1; HRMS calcd for $\text{C}_{38}\text{H}_{28}\text{N}_2$ 512.2252, found 512.2250. Anal. Calcd for $\text{C}_{38}\text{H}_{28}\text{N}_2$: C 89.03, H 5.51, N 5.46. Found: C 89.09, H 5.63, N 5.38.

Acknowledgment. We thank National Science Council, Taiwan, for financial support of this work.

Supporting Information Available: Detailed synthesis procedure, spectral data, NMR spectra, and Maldi-Mass of new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.