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Studies on the Structure of *N*-Phenyl-Substituted Hexaaza[1_6]paracyclophane: Synthesis, Electrochemical Properties, And Theoretical Calculation

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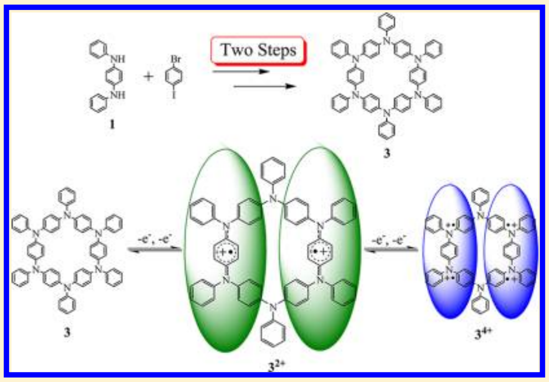
S *Supporting Information*

ABSTRACT: The *N*-phenyl-substituted hexaaza[1_6]paracyclophane (**3**, hexamer) has been synthesized successfully in two steps and the noncoplanar conformation was calculated by Gaussian program. The electrochemical properties exhibited lots of interesting results and each overlapping oxidative wave contained two-electron transfer.



INTRODUCTION

Oligoarylamines usually contain two or more oxidized forms so that these compounds are widely used in hole-transporting layer of OLEDs.[1,2] With the increase in redox center and aromatic-bridge conjugation, electron-transfer phenomena and oxidized states of oligoarylamines have been widely investigated by electrochemical and optical methods.[3−7] Linear[6] and star-shaped[5,7] oligoarylamines have attracted most interest with their outstanding molecular-based electronic properties in recent years. So far, cyclic oligoarylamines have not yet been generally studied because of difficulties in the synthesis and purification of these compounds.[8−10] Although the synthesis of some hexaaza[1_6]paracyclophane derivatives, cyclic oligoarylamines, had been reported in a patent issued in 1993,[10] the indentification and characteristic data were not described. The *N*-anisyl-substituted hexaaza[1_6]paracyclophane was studied by Ito et al.,[4a] but the procedure for the synthesis consisted of more than three steps. To stabilize the hexaaza[1_6]-paracyclophane, the anisyl group was used on the *para*-position substituent. Five redox couples were observed in the oxidation part, and the optimized structure showed that this hexaaza-[1_6]paracyclophane is coplanar by theoretical calculations.

In this study, we have successfully synthesized *N*-phenyl-substituted hexaaza[1_6]paracyclophane (**3**, hexamer) in two steps, starting with *N,N*′-diphenyl-*p*-phenylenediamine (**1**, Scheme 1). Ullmann-type coupling reaction of **1** with 1-bromo-4-iodobenzene provided *p*-phenylenediamine **2** (PD-Br).[11] Then, treatment of **2** with *t*-BuONa in the presence of a catalytic amount of Pd(0) complex[12] resulted in the self-coupling of the reactant and the formation of the title compound (**3**, hexamer). In order to rationalize the mass spectrum of **3**, the molecular model study on the fragmentation of the structure of this compound was carried out as follows. At first, a fragment of phenyl (C_6H_5) or *N*-phenyl (NC_6H_5) group was removed piece by piece, starting from the parent structure (**3**, hexamer). Then, after each time when a C_6H_5 or NC_6H_5 piece was removed, the m/z value of the remained species was calculated and listed in Table S1 (Supporting Information). It was found that the corresponding m/z values of the mass spectrum matched very well to those listed in Table S1, confirming the exact structure of the hexamer (**3**).

In order to confirm that the hexamer (**3**) was the cyclic oligoarylamine, linear **N6** (**6**), a similar compound which contained six nitrogen atoms and was connected with phenyl groups, was also synthesized (Scheme 2) and characterized by spectral and electrochemical methods. The fragment of the phenyl (C_6H_5), *N*-phenyl (NC_6H_5), or diphenylamine ($C_6H_5NC_6H_5$) group was removed in a stepwise fashion from linear **N6**. When a C_6H_5, NC_6H_5, or $C_6H_5NC_6H_5$ piece was removed, the m/z value of the remained species was calculated and listed in Table S2 (Supporting Information). Furthermore, we herein report the electrochemical behaviors and spectral changes of the hexamer (**3**) and linear **N6**.

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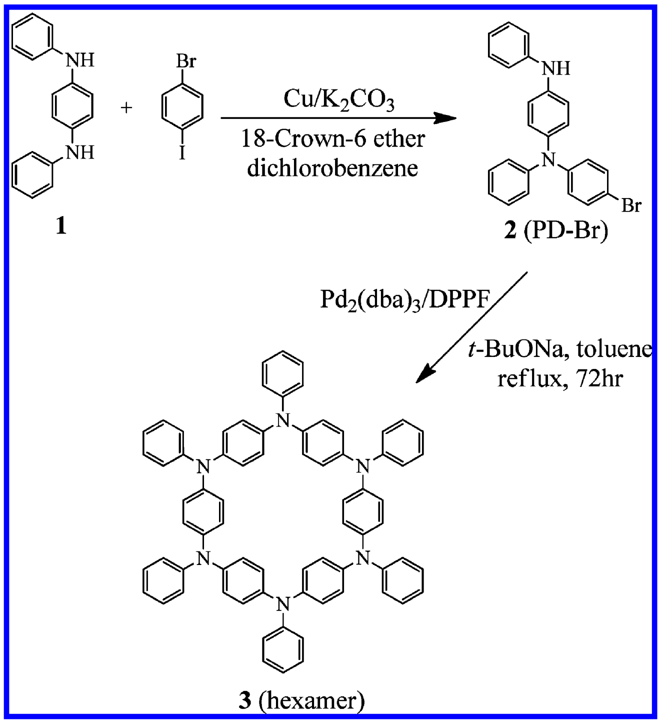
Scheme 1. Synthesis Pathway of the *N*-Phenyl-Substituted Hexaaza[1_6]paracycphane (3, Hexamer)



■ RESULTS AND DISCUSSION

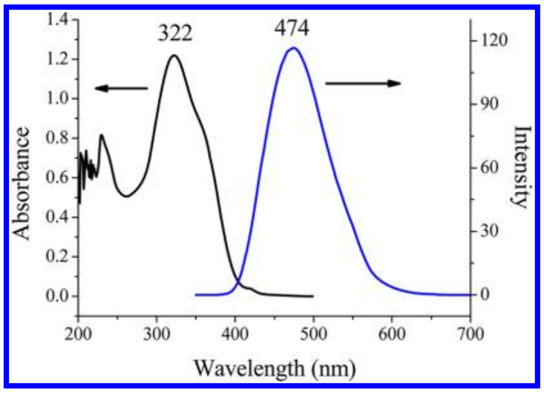


Figure 1. Absorption (black line) and emission (blue line) spectra of the hexamer (3) (excitation wavelength = 322 nm).

Figure 1 shows the room-temperature absorption (black line) and emission (blue line) spectra of the hexamer (**3**) in CH_2Cl_2. The hexamer (**3**) exhibited a characteristic absorption at 322 nm. When the hexamer (**3**) was excited at 322 nm, an emission at 474 nm (a blue light) was observed. On the other hand, the absorption peak and the emission band of the linear **N6** were at 338 and 495 nm, respectively (Figure 2).

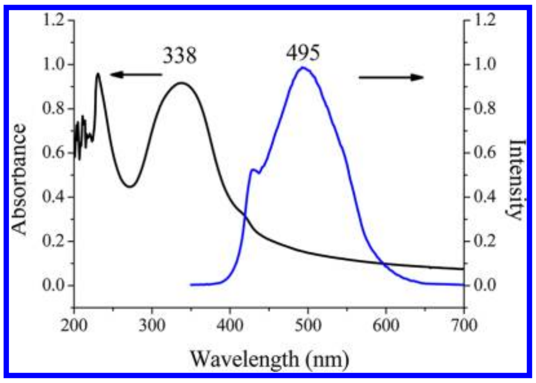
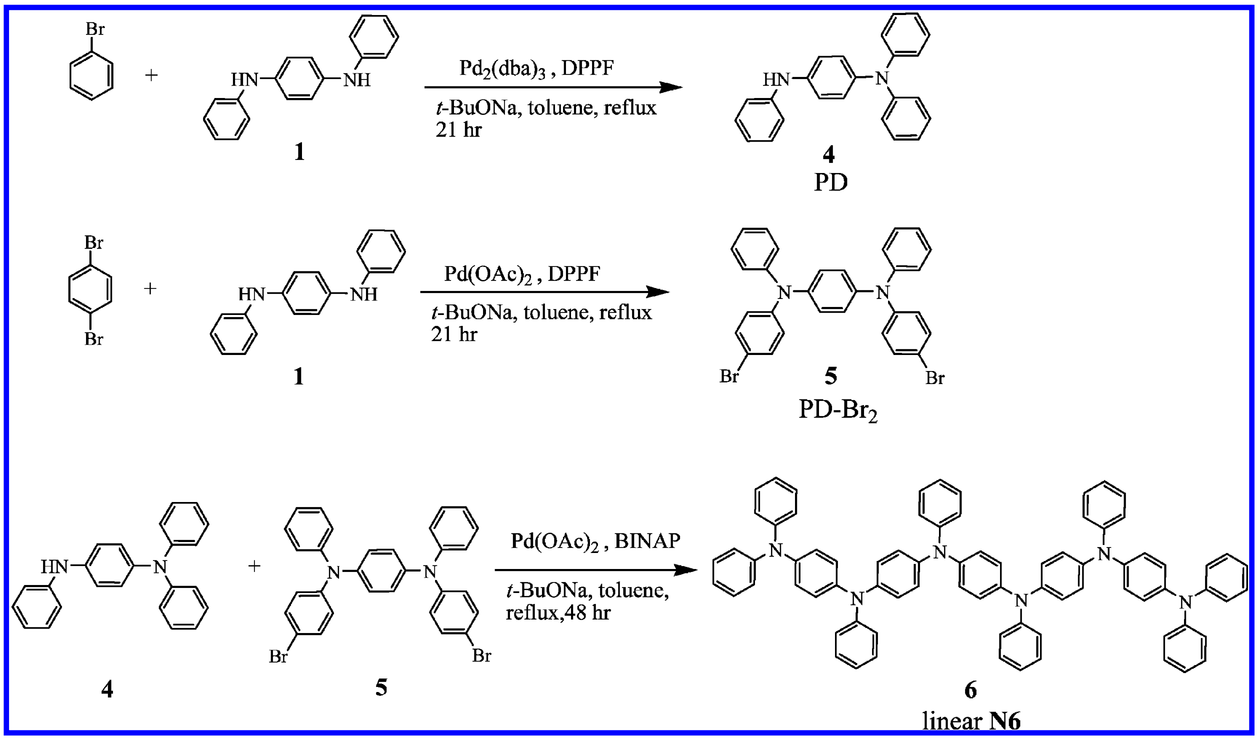


Figure 2. Absorption (black line) and emission (blue line) spectra of linear **N6** (excitation wavelength = 338 nm).

Scheme 2. Synthesis Pathway of the Linear N6 (6)



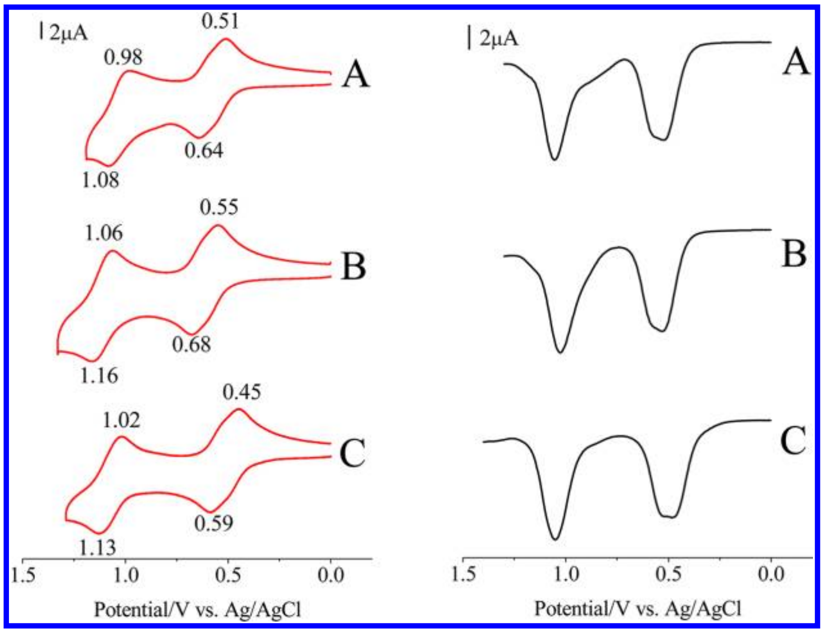


Figure 3. Cyclic voltammetry (left) and differential pulse voltammetry (right) of 1.0 × 10^{-3} M hexamer (**3**) in CH_2Cl_2 containing 0.1 M (A)TBABF$_4$, (B) TBAP, and (C)TBAPF$_6$. Working electrode: glassy carbon. Scan rate: 0.1 V/s ($Fc^{+/0}$ = +0.54 V).

The left half part of Figure 3 shows the cyclic voltammogram (CV) of the hexamer (**3**) with different electrolytes in CH_2Cl_2. In the oxidation process, two oxidation waves were observed at E_{pa} = +0.68 and +1.16 V (E_{pc} = +0.55 and +1.06 V, respectively) (Figure 3B, left) in TBAP/CH_2Cl_2. Both oxidative waves appeared to be the overlapping of two redox couples. To probe the anion effect, TBABF$_4$ and TBAPF$_6$ were also used as the electrolyte (Figure 3A,C, left). Upon the change of electrolyte, these two oxidative waves moved cathodically and the ΔE between first wave and second wave were also changed. The ΔE_{pa}'s are +0.44, +0.48 and +0.54 V for TBABF$_4$, TBAP, and TBAPF$_6$ as electrolytes, respectively. It indicates that the interaction between the oxidized hexamer and electrolyte anion decreased in the order BF_4^- > ClO_4^- > PF_6^- (the order of size of anions was BF_4^- < ClO_4^- < PF_6^-).[13]

To further resolve the electron-transfer number of the first oxidation wave, controlled potential coulometry (CPC) and differential pulse volammetry (DPV) were carried out. Controlled potential coulometry (Figure 4) of 1.0 × 10^{-6} mol of hexamer (**3**) at +0.84 V indicated that two electrons per molecule were removed in TBAP/CH_2Cl_2.[7b,14]

Differential pulse voltammetry, as shown in the right half of Figure 3, was used to identify the number of electrons oxidized by calculating each integration area (Table 1). The integration areas of peaks (Figure 3B, right) were 1.17 × 10^{-7} VA (first wave) and 1.18 × 10^{-7} VA (second wave), respectively. As indicated by the results of the electrochemical experiments, the hexamer (**3**) has totally four-electron transfer in the oxidations, and each oxidative wave has two-electron transfer. The CV and DPV of the linear **N6** were shown in Figure 5. Six oxidation waves were observed at E = +0.48, +0.74, +0.96, +1.14, +1.21 and +1.33 V in the DPV. The CV and DPV of linear **N6** were obviously different from those of the hexamer (**3**). According to the electrochemical studies, the results were another evidence that the hexamer (**3**) is a cyclic oligoarylamine.

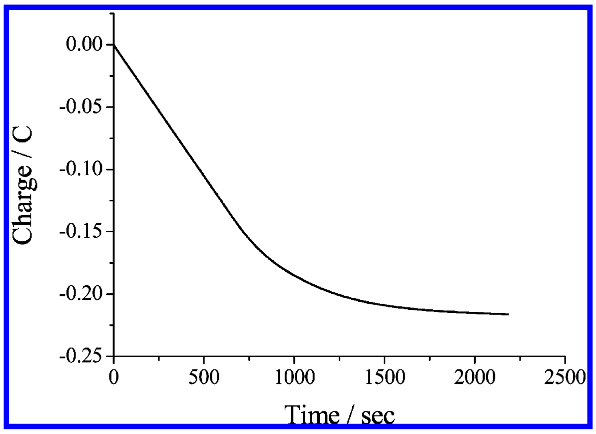


Figure 4. Controlled potential coulometry at E_{appl} = +0.84 V vs Ag/AgCl for the hexamer (**3**) (1.0 × 10^{-6} mol) in CH_2Cl_2 (0.1 M TBAP).

Table 1. Integration Areas of Peaks with Different Electrolytes in Differential Pulse Voltammograms

electrolyte	second peak	first peak
TBAP	1.18 × 10^{-7}	1.17 × 10^{-7}
TBABF$_4$	1.45 × 10^{-7}	1.33 × 10^{-7}
TBAPF$_6$	1.16 × 10^{-7}	1.17 × 10^{-7}

The digital simulation[15] of experimental CV (Figure 6) was carried out to distinguish the overlapping redox couples from the two oxidation waves (Figure 3B). The reaction mechanism was presented in Table 2. The $E_{1/2}$ of the first overlapping oxidative wave were +0.54 (E_1^{ox}), +0.65 (E_2^{ox}) and +1.07 (E_3^{ox}), +1.14 (E_4^{ox}) V for the second overlapping oxidative wave in the simulated results. The simulated CV of the hexamer (**3**) has excellent agreement with experimental CV.

The characteristic absorption peak of the hexamer (**3**) at 322 nm had a molar extinction coefficient of 4.2 × 10^3 M^{-1} cm^{-1}. In the potential range of E_{appl} = +0.00 to +0.67 V, the spectra at equilibrium were obtained (Figure 7A). As the potential was moved anodically, the 322 nm peak of neutral hexamer (**3**) gradually decreased in absorbance. At the same time, new absorption peaks at 400 and 836 nm gradually increased. The absorption at 836 nm was an intervalence charge-transfer (IV-

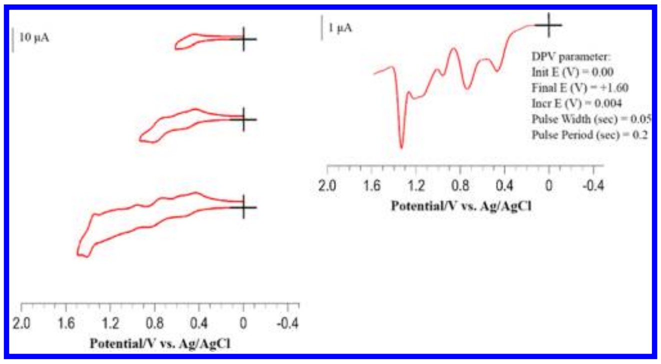


Figure 5. Cyclic voltammetry (left) and differential pulse voltammetry (right) of 1.0 × 10^{-3} M linear **N6** in CH_2Cl_2 containing 0.1 M TBAP. Working electrode: glassy carbon. Scan rate: 0.1 V/s.

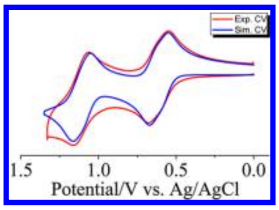


Figure 6. Experimental (red) and simulated (blue) CV of 1.0 × 10^{-3} M hexamer (**3**) (TBAP/CH_2Cl_2). Working electrode: glassy carbon disk (area = 0.07 cm^2). Scan rate: 0.1 V/s.

Table 2. Reaction Mechanism of the Hexamer (3) (TBAP/CH_2Cl_2) in the Simulated CV

	electrochemical reactions	E^0 (V)
E_1^{ox}	$(hexamer)^+ + e = (hexamer)$	+0.54
E_2^{ox}	$(hexamer)^{2+} + e = (hexamer)^+$	+0.65
E_3^{ox}	$(hexamer)^{3+} + e = (hexamer)^{2+}$	+1.07
E_4^{ox}	$(hexamer)^{4+} + e = (hexamer)^{3+}$	+1.14

CT) band.[16] In another potential range of E_{appl} = +0.79 to +1.11 V (Figure 7B), the absorbances 400 and 836 nm decreased dramatically. A new peak grew at 586 nm.

The spectral change of the hexamer (**3**) in different oxidation states was similar to that of *N,N,N′,N′*-tetraphenylphenylenediamine (TPPD) (Figure 8).[16b,17] As the potential shifted positively, it was observed that the characteristic peak (312 nm) of TPPD gradually decreased, a new peak at about 408 nm and a broad band at λ_{max} = 856 nm in the near-IR region were formed. When the applied potential was further moved anodically, the absorbances of $TPPD^+$ decreased and a new band grew up at 598 nm. It is thus inferred that two cation radical were separately localized at two TPPD units bridged by two phenylnitrido moieties when the hexamer (**3**) was oxidized to a dication state (Scheme 3) and the cation radicals appears nearly independent to each other. Further oxidation by two electrons generates two units of $TPPD^{2+}$. It is worthy to note that the absorbance between 1200 to 1700 nm decreased after E_{appl} = +0.58 V (Figure 7A). It suggested that a weak IV-CT band via the phenylnitrido (NC_6H_5) units was existed in the low energy region[18] and also confirmed the cyclic structure of the hexamer (**3**) (two TPPD conformation was connected by NC_6H_5 bridges). The weak energy transfer through the NC_6H_5 bridge was unusual (Scheme 3).

In order to confirm the hexamer (**3**) conformation, we seek help from theoretical calculations. The optimized structure of hexamer (**3**) calculated based on B3LYP/6-31G** level with the GAUSSIAN 09 program shows that the hexamer (**3**) was not coplanar (Figure 9).[19] The angles between phenyl rings R1−R2, R3−R2, and R3−R4 are 58.2°, 84.9°, and 84.8° (Table 3), respectively, which make the environment of N1 atom different from those of N2 and N3 atoms. That is, the electronic interaction between NC_6H_5 bridge and TPPD unit is minimal due to nearly perpendicular angles. This explains why the oxidation behavior of the hexamer (**3**) is similar with that of TPPD.

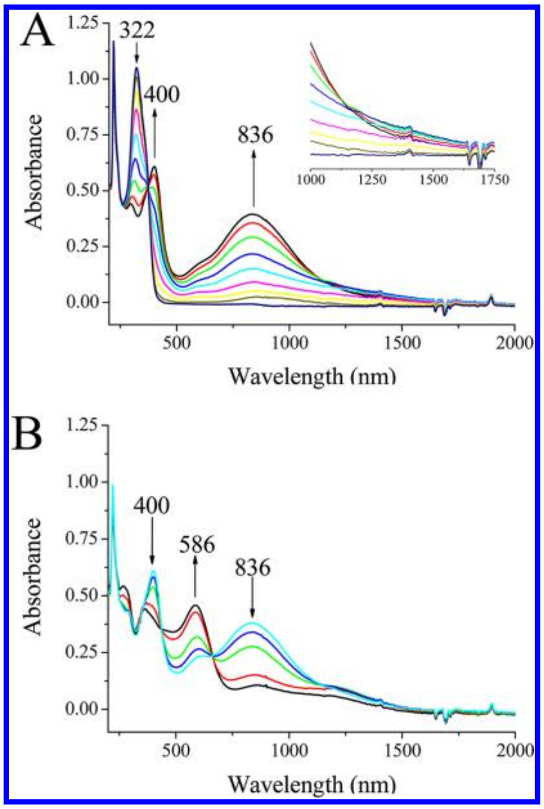


Figure 7. Spectral changes of 2.5 × 10^{-4} M hexamer (**3**) in CH_2Cl_2 containing 0.1 M TBAP at various applied potentials. E_{appl} = (A) +0.00 to +0.67; (B) +0.79 to +1.11 V.

The spectral change of the linear **N6** at various applied potentials were also studied (Figure 10, 11), and the results were obviously different from the hexamer (**3**). The spectral changes of linear **N6** are shown in Figures 10 and 11. In the potential range of E_{appl} = +0.00 to +0.57 V, the first step oxidation spectrum of linear **N6** were obtained (Figure 10A). As the potential shifted anodically, the characteristic absorption at 338 nm gradually decreased while two new peaks (314 and 438 nm) and a broad band at 1420 nm grew. In another potential range of E_{appl} = +0.70 to +0.90 V (Figure 10B) (the second step oxidation spectrum), the absorbance at 314 nm decreased dramatically. The broad band (1320 nm) in the near-IR region grew. When the electrode potential ranging from +0.93 to +1.10 V was applied (Figure 11A), the third step oxidation spectral changes were obtained, two new absorption peaks at 630 and 910 nm gradually increased and the absorbance at 1320 nm decreased. If the applied potential was further increased, from +1.25 to +1.50 V, the absorbance at 430, 590, and 910 nm decreased (Figure 11B).

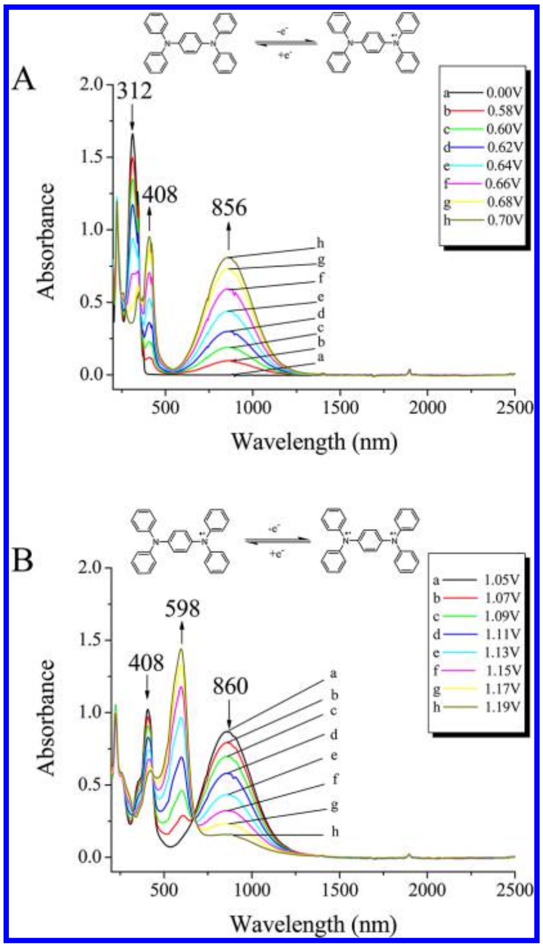


Figure 8. Spectral change of 2.5×10^{-4} M TPPD at various applied potenials in CH_2Cl_2 containing 0.1 M TBAP.

■ CONCLUSION

In conclusion, we have successfully synthesized the hexamer (**3**) by a two-step synthesis method. A blue light emission at 474 nm of hexamer (**3**) was obtained. The hexamer (**3**) has multiple redox potential and exhibits different interactions with different electrolyte. Each of the oxidation processes was reversible and stable after potential cycling continuously in CH_2Cl_2. The results of the hexamer (**3**) and linear **N6** exhibit entirely different physical properties. According to these results, the hexamer (**3**) has the potential for the hole-transporting layer of light-emitting device.[8b,10]

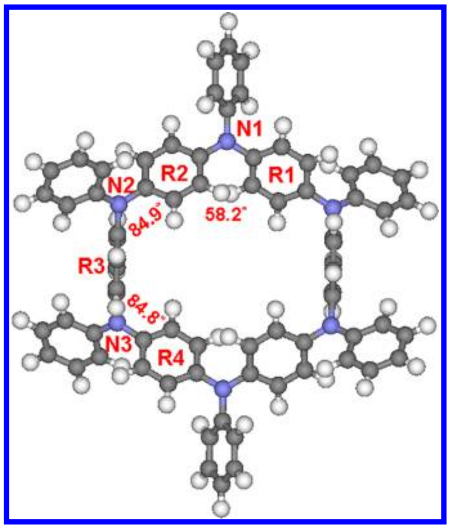


Figure 9. Optimized structure and angles between phenyl rings of the hexamer (**3**) calculated based on B3LYP/6-31G** level: Key: N, blue; C, gray; H, white.

■ EXPERIMENTAL SECTION

N^1-(4-bromophenyl)-N^1,N^4-diphenylphenylenediamine (2, PD-Br). N^1-(4-Bromophenyl)-N^1,N^4-diphenylphenylenediamine (**2**, PD-Br) was synthesized by Ullmann coupling reaction.[16] A mixture of N^1,N^4-diphenylphenylenediamine (**1**) (2 g, 7.7 mmol), 4-bromoiodobenzene (1 g, 3.5 mmol), copper powder (0.25 g, 3.9 mmol), potassium carbonate (0.54 g, 3.9 mmol), and 18-crown-6 ether (0.01 g) in 1,2-dichlorobenzene (10 mL) was heated under N_2 atmosphere at reflux temperature for 3 h. The reaction mixture was then filtered. The filtrate was evaporated under vacuum, and the crude product was purified by column chromatography on silica gel by using dichloromethane/hexane (1:2) as the eluent to give PD-Br (**2**) as a green syrup (340 mg, 11%): UV/vis (CH_2Cl_2) λ_{max}/nm 314; MS (FAB$^+$) m/z = 415.368 ([M + H]$^+$); ^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm) 7.32 (4H, J = 7.2 Hz, d), 7.28−7.26 (4H, m), 7.10−7.00 (8H, m), 6.93 (4H, J = 6.0 Hz, d), 5.78 (NH, s); ^{13}C NMR (150 MHz, CD_2Cl_2) δ (ppm) 147.7, 147.5, 143.5, 140.6, 139.7, 132.0, 129.5, 129.4, 127.1, 124.1, 123.9, 123.7, 122.8, 120.8, 119.2, 117.4, 113.7. Anal. Calcd for $C_{24}H_{19}N_2Br$: C, 69.41; H, 4.61; N, 6.74. Found: C, 69.26; H, 4.88; N, 6.75.

***N*-Phenyl-Substituted Hexaaza$[1_6]$paracyclophane (3, Hexamer).** Hexamer **3** was synthesized by heating at reflux temperature a stirred solution of PD-Br (**2**, 0.22 g, 0.53 mmol), $Pd_2(dba)_3$ (15 mg, 0.016 mmol), dppf (18 mg, 0.032 mmol), and Na^{t}OBu (80 mg, 0.83 mmol) in toluene (50 mL) under N_2 atmosphere for 72 h. The reaction mixture was filtrated, and the filtrate was evaporated under vacuum. The crude product was washed by hexane and methanol to give hexamer **3** as a light yellow solid (140 mg, 26.3%): UV/vis (CH_2Cl_2) λ_{max}/nm 322; FT-IR (KBr, cm^{-1}) 2922, 2856, 1594, 1491,

Scheme 3. Oxidation State of the Hexamer (3)

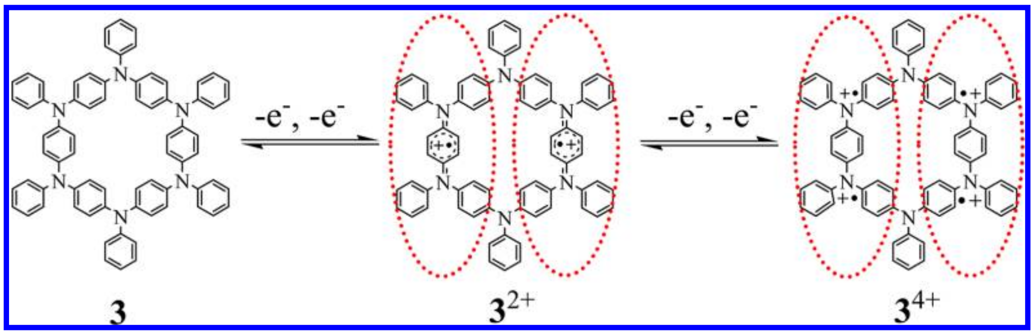


Table 3. Mulliken Charges and Angles between Phenyl Rings of Hexamer (3) Calculated on the Basis of B3LYP/6-31G** Level

Mulliken charges								
N1	N2	N3	N4	N5	N6	R1	R2	R3
−0.653	−0.657	−0.657	−0.653	−0.657	−0.657	+0.455	+0.455	+0.440
R4	R5	R6	R7	R8	R9	R10	R11	R12
+0.455	+0.455	+0.440	+0.226	+0.122	+0.122	+0.226	+0.122	+0.122
angles (deg)								
R1−R2	R1−R7	R2−R7	R2−R3	R2−R8	R3−R8	R3−R4	R3−R9	R4−R9
58.2	71.4	71.4	84.9	75.9	74.7	84.8	74.8	75.8
R4−R5	R4−R10	R5−R10	R5−R6	R5−R11	R6−R11	R6−R1	R6−R12	R1−R12
57.8	71.1	71.7	84.6	75.7	74.8	84.6	74.7	75.8

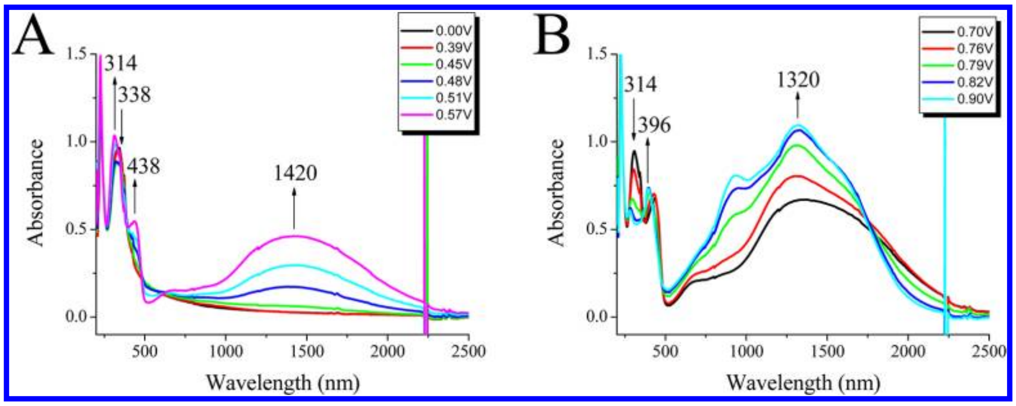


Figure 10. Spectral change of (A) first and (B) second oxidation steps with 2.5 × 10^{-4} M linear **N6** at various applied potenials in CH_2Cl_2 containing 0.1 M TBAP.

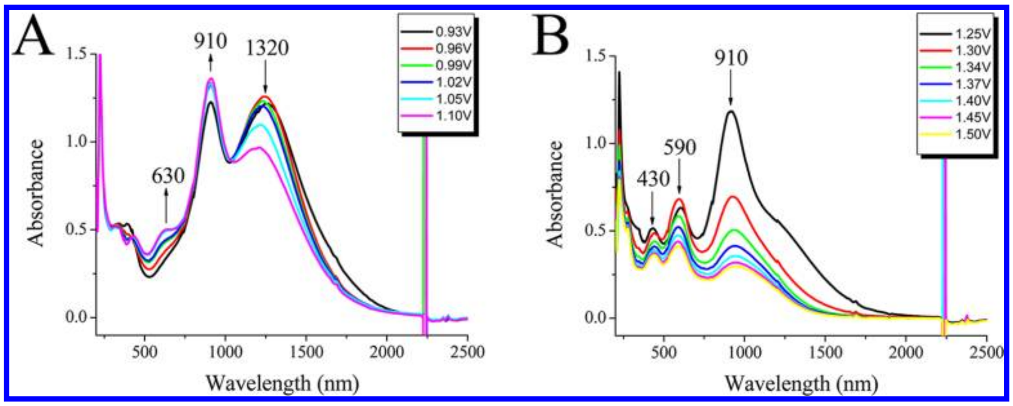


Figure 11. Spectral change of (A) third and (B) fourth oxidation steps with 2.5 × 10^{-4} M linear **N6** at various applied potenials in CH_2Cl_2 containing 0.1 M TBAP.

1272; mp 201−202 °C; HRMS (FAB^+) *m*/*z* calcd for $C_{72}H_{55}N_6$ ($[M + H]^+$) 1003.4492, found 1003.4498; ^1H NMR (600 MHz, CD_2Cl_2) δ (ppm) 7.45 (d, *J* = 8.4 Hz, 6H), 7.25 (t, *J* = 7.2 Hz, 12H), 7.06 (d, *J* = 16.8 Hz, 24H), 6.98 (s, 12H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ (ppm) 129.4, 129.3, 127.2, 126.9, 123.4, 123.1, 122.3, 120.6, 119.4, 117.2. Anal. Calcd for $C_{72}H_{54}N_6$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.05; H, 5.65; N, 8.21.

***N*¹-(4-Phenyl)-*N*¹,*N*⁴-diphenylbenzene-1,4-diamine (4, PD).** A mixture of N^1,N^4-diphenylphenylenediamine (**1**, 3.905 g, 15 mmol), bromobenzene (0.785 g, 5 mmol), $Pd_2(dba)_3$ (27 mg, 0.03 mmol), dppf (34 mg, 0.06 mmol), and Na^tOBu (1.44 g, 15 mmol) in toluene (100 mL) was heated under N_2 atmosphere at reflux temperature for 21 h. The reaction mixture was then filtered. The filtrate was evaporated under vacuum and the crude product was purified by column chromatography on silica gel by using dichloromethane/hexane (1:2) as the eluent to give PD (**4**) as a white solid (0.5 g, 30%): mp 142−143 °C; ^1H NMR (600 MHz, DMSO-d_6) δ (ppm) 7.26−7.18 (m, 6H), 7.08−7.03 (m, 4H), 6.97−6.61 (m, 8H), 6.82−6.77 (t, *J* = 15.0 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm) 147.7, 143.6, 140.0, 139.1, 129.3, 129.2, 127.0, 122.2, 121.8, 119.5, 118.2, 116.5.

***N*¹,*N*⁴-bis(4-bromophenyl)-*N*¹,*N*⁴-diphenylbenzene-1,4-diamine (5, PD-Br₂).** A mixture of N^1,N^4-diphenylphenylenediamine (**1**, 0.5 g, 1.9 mmol), 1,4-dibromobenzene (4.5 g, 19 mmol), $Pd(OAc)_2$ (17 mg, 4% mol), dppf (63 mg, 6% mol), and Na^tOBu (1.83 g, 19 mmol) in toluene (30 mL) was heated under N_2 atmosphere at reflux temperature for 21 h. The reaction mixture was then filtered. The filtrate was evaporated under vacuum and the crude product was purified by column chromatography on silica gel by using dichloromethane/hexane (1:4) as the eluent to give PD-Br_2 (**5**) as a white solid (0.52 g, 48%): mp 228−229 °C; HRMS (EI^+) *m*/*z* calcd for $C_{30}H_{22}Br_2N_2$ (M^+) 568.0150, found 568.0157; ^1H NMR (600 MHz, CD_2Cl_2) δ (ppm) 7.33 (d, *J* = 10.2 Hz, 4H), 7.27 (t, *J* = 9.0 Hz, 4H), 7.09 (d, *J* = 9.0 Hz, 4H), 7.03 (t, *J* = 9.0 Hz, 2H), 6.97−6.94 (m, 8H);

^{13}C NMR (150 MHz, CD_2Cl_2) δ (ppm) 147.4, 147.2, 142.9, 132.2, 129.5, 125.9, 124.7, 124.4, 123.3, 114.4. Anal. Calcd for $C_{30}H_{22}Br_2N_2$: C, 63.18; H, 3.89; N, 4.91. Found: C, 62.70; H, 3.62; N, 4.90.

Linear N6 (6). Linear **N6** (**6**) was synthesized by heating at reflux temperature a stirred solution of PD-Br_2 (**5**, 0.257 g, 0.451 mmol), $Pd(OAc)_2$ (20 mg, 0.3% mol), BINAP (70 mg, 0.4% mol), PD (0.38 g, 1.13 mmol), and Na^{t}OBu (0.35 g, 3.61 mmol) in toluene (50 mL) under N_2 atmosphere for 48 h. The reaction mixture was filtrated, and the filtrate was evaporated under vacuum and washed with MeOH and acetone to give linear N6 (**6**) as a gray solid (0.195 g, 40%): UV/vis(CH_2Cl_2) λ_{max}/nm 338; mp 334−335 °C; MS (FAB$^+$) m/z calcd $C_{78}H_{60}N_6$ ([M + H]$^+$) 1081.235, found 1081.488; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.23 (t, J = 15.3 Hz, 24H), 7.09 (d, J = 14.4 Hz, 16H), 7.01−6.98 (m, 20H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 129.3, 125.3, 123.9. Anal. Calcd for $C_{78}H_{60}N_6$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.59; H, 5.65; N, 7.67.

Organic solvents were degassed by purging with prepurified nitrogen gas and dried before use. Analytical grade tetra-*n*-butylammonium perchlorate (TBAP) was obtained from ACROS and recrystallized twice from ethyl acetate and then dried in vacuo prior to use.

A mass spectrometry experiment for the hexamer was carried out with a high-resolution mass spectrometer. The ion source was generated by fast atom bombardment (FAB). By using a xenon laser, desorption of the analyte was operated. The acceleration voltage for the operation of a positive-ion mode was 3 kV. The magnetic sector mass analyzer was used for the HRMS measurements. Electrochemistry was performed with a CHI Model 660 series electroanalytical workstation. Cyclic voltammetry was conducted with the use of a three-electrode cell in which a glassy carbon electrode (area = 0.07 cm^2) was used as working electrode. The glassy carbon electrode was polished with 0.05 μm alumina on Buehler felt pads and was ultrasonicated for 1 min to remove the alumina residue. The auxiliary electrode is a platinum wire, and the reference electrode is a homemade Ag/AgCl, KCl(satd) reference electrode. The spectroelectrochemical cell was composed of a 1 mm cuvette, a platinum gauze thin layer as working electrode, a platinum wire as auxiliary electrode, and an Ag/AgCl, KCl(satd) reference electrode. Absorption spectra were measured with a UV/vis/near-IR spectrophotometer. ^{1}H NMR spectra were obtained with a 600 WB spectrometer. The fluorescence spectrum was recorded on a spectrofluorometer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Calculated energy results for compound **3**, copies of ^{1}H and ^{13}C NMR spectra for compounds **2**, **3**, and **6**, UV−vis spectrum for compound **3**, and mass spectra for compounds **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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