Ferromagnetic Spin Alignment in Head-to-Tail Coupled Oligo(1,4-phenyleneethynylene)s and Oligo(1,4-phenylenevinylene)s Bearing Pendant *p*-Phenylenediamine Radical Cations

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Received April 12, 2000

The intramolecular and long-range ferromagnetic coupling between *p*-phenylenediamine radical cations in head-to-tail coupled oligo(1,4-phenyleneethynylene)s and oligo(1,4-phenylenvinylene)s between neighbors and next-nearest neighbors is described. UV/vis/near-IR experiments show that the radical cations are localized in the pendant *p*-phenylenediamine units of the conjugated oligomers. The ESR spectra of these oligo(1,4-phenyleneethynylene) and oligo(1,4-phenylenvinylene) di(radical cation)s are consistent with those of a triplet state. A linear behavior is observed for the doubly integrated ESR intensity of the $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ signals with the inverse temperature ($I \sim 1/T$), consistent with Curie's law. This behavior indicates a triplet ground-state diradical with a large triplet−singlet energy gap or possibly a degeneracy of singlet and triplet states.

Introduction

In the past decade the interest in organic magnetic materials has increased dramatically.[1] Various efforts have focused on preparing high-spin polyradicals by creating an alternating sequence of spin-carrying and ferromagnetic-coupling units in linear, branched, hyperbranched, and network topologies.[1] Considerable progress in the spin value of these polyradicals can be noted in recent years. Iwamura et al. have obtained a spin quantum number of $S = 9$ for branched oligocarbenes,[2] and more recently Rajca et al. used triarylmethylradicals in a well-defined dendritic macrocycle and in a π-conjugated hydrocarbon network to achieve spin quantum numbers as high as $S = 10$ and $S \geq 40$, respectively.[3,4]

Because of their unusual stability and convenient generation by one-electron oxidation, arylamine radical cations have recently been considered in studies on magnetic organic materials.[5−8] Especially the use of *p*-phenylenediamine units, oxidized to the corresponding radical cations, allows for an advantageous combination of generation, stability, and ferromagnetic coupling when the nitrogen atoms are used to link the radical centers.[6] Moreover, the synthesis of arylamines has witnessed a tremendous progress in recent years using palladium-catalyzed C−N coupling reactions as developed by Hartwig et al. and Buchwald et al.[9] These improvements have resulted in the preparation of novel high-spin molecules.[10,11]

Employing an alternating *meta*−*para* topology of oligoanilines carrying hydrogen, methyl, or phenyl substituents, we have been able to generate high-spin di-, tri-, and tetra(radical cations) in linear and branched systems as model compounds for so-called polaronic ferromagnets.[6,10] However, in extending these linear and branched polyarylamines, a problem may arise when incomplete oxidation of the *p*-phenylenediamine unit occurs, because such spin defects are detrimental for achieving a high spin state, especially when the spin-carrying unit is part of the main coupling pathway. To overcome this problem it is possible to use a π-conjugated backbone as a coupling unit with pendant radical groups.[12−14] To ensure ferromagnetic coupling between the spin-bearing units of a pendant polyradical, it is necessary to carefully control the topology of the substitution pattern along the polymer

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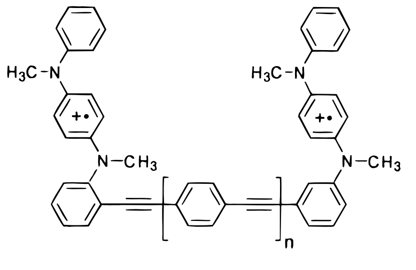
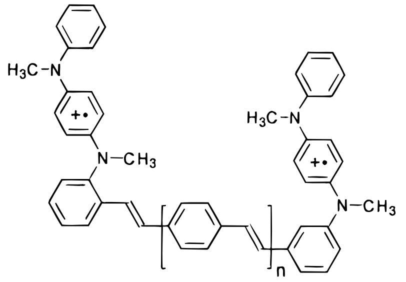
10.1021/jo000548o CCC: $19.00

chain in order to guarantee the in-phase periodicity of spin polarization between adjacent radicals but also between nonadjacent radicals. The advantage of such polymers is that they will be less sensitive to spin defects, because ferromagnetic coupling between next-nearest neighbors is maintained via the π-conjugated backbone. Indeed, Nishide et al.[14a−c] demonstrated that for 1,2- and 1,4-phenylenevinylene-based diradicals there is intrachain spin coupling between next-nearest neighbors.



n = 0 : $6^{2\bullet 2+}$

n = 1 : $7^{2\bullet 2+}$

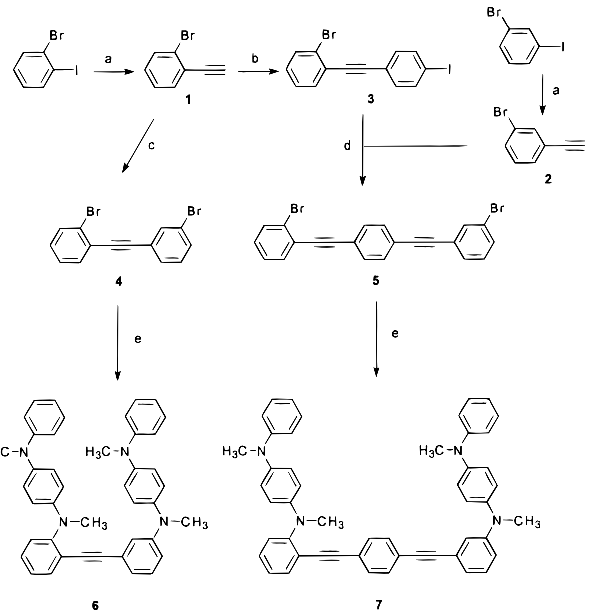


n = 0 : $13^{2\bullet 2+}$

n = 1 : $14^{2\bullet 2+}$

Here we report on the synthesis and characterization of novel oligo(1,4-phenyleneethynylene)s ($6^{2\bullet 2+}$ and $7^{2\bullet 2+}$) and oligo(1,4-phenylenevinylene)s ($13^{2\bullet 2+}$ and $14^{2\bullet 2+}$) carrying pendant *p*-phenylenediamine radical cations in a regioregular substitution pattern. The head-to-tail coupled oligomers $6^{2\bullet 2+}$ and $13^{2\bullet 2+}$ ($n = 0$) were designed to investigate whether ferromagnetic coupling occurs between neighboring pendant *p*-phenylenediamine radical cations attached to *p*-phenyleneethynylene and *p*-phenylenevinylene chains, in a topology that favors the in-phase periodicity of spin polarization at the nitrogen atoms. The extended oligomers $7^{2\bullet 2+}$ and $14^{2\bullet 2+}$ ($n = 1$), in which the two radical cations are connected by a π-conjugated chain that incorporates an additional spinless monomeric unit, model pendant polyradicals in which spin−spin interaction can only occur between next-nearest neighbors We demonstrate using variable temperature ESR that the di(radical cations) of these head-to-tail coupled conjugated oligomers indeed possess a low-energy triplet state.

Scheme 1[a]



[a] Reagents: (a) i: trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, ii: TBAF, THF; (b) 1,4-diiodobenzene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N; (c) 3-bromoiodobenzene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N; (d) compound **2**, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N; (e) $Pd_2(dba)_3$, DDPFA, NaO*t*Bu, *N,N'*-dimethyl-*N*-phenyl-1,4-benzenediamine.

Results and Discussion

Synthesis of Model Compounds. For the preparation of **6** and **7** (Scheme 1), 2-bromoiodobenzene was reacted with trimethylsilylacetylene to give 1-ethynyl-2-bromobenzene **1** after deprotection. Reaction of **1** with either 3-bromoiodobenzene or 1,4-diiodobenzene yielded 2,3'-dibromodiphenylacetylene **4** and 2-bromo-4'-iododiphenylacetylene **3**, respectively. Compound **3** was then reacted with 1-ethynyl-3-bromobenzene **2** (synthesized in the same manner as **1**), to yield 3,3''-dibromodiphenyldiacetylene **5**. The desired model compounds **6** and **7** were obtained from **4** and **5** by reaction with *N,N'*-dimethyl-*N*-phenyl-1,4-benzenediamine[10] using sodium *tert*-butoxide as a base and tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 1 mol %) and (−)-(*R*)-*N,N'*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine (DDPFA, 3 mol %) as the catalyst.[9] Compounds **6** and **7** were isolated by column chromatography (SiO_2; dichloromethane-heptane, 1:1) in 53% and 65% yields, respectively.

Tetraamines **13** and **14** were synthesized as shown in Scheme 2. 2-Bromobenzaldehyde was reacted with (3-bromobenzyl)triphenylphosphonium bromide **8** to give 1-(2-bromophenyl)-2-(3-bromophenyl)ethene **10**. (2-Bromobenzyl)triphenylphosphonium bromide **9** was reacted with terephthaldicarboxaldehyde to give 1-(2-bromophenyl)-2-(4-formylphenyl)ethene **11**, which was subsequently reacted with (3-bromobenzyl)triphenylphosphonium bromide **8** to give dibromide **12**. Dibromides **10** and **12** were reacted with *N,N'*-dimethyl-*N*-phenyl-1,4-benzenediamine[10] using the $Pd_2(dba)_3$/DDPFA catalyst system as described for **6** and **7**, to provide **13** and **14** in 67% and 38% yield, respectively, after isolation by column chromatography (SiO_2; dichloromethane−heptane, 1:1).

Redox Properties. The cyclic voltammograms of **6** and **7** show two chemically reversible oxidation waves at E^0_1 and E^0_2 (Figure 1a, Table 1). The close correspondence of the oxidation potentials of **6** and **7** with

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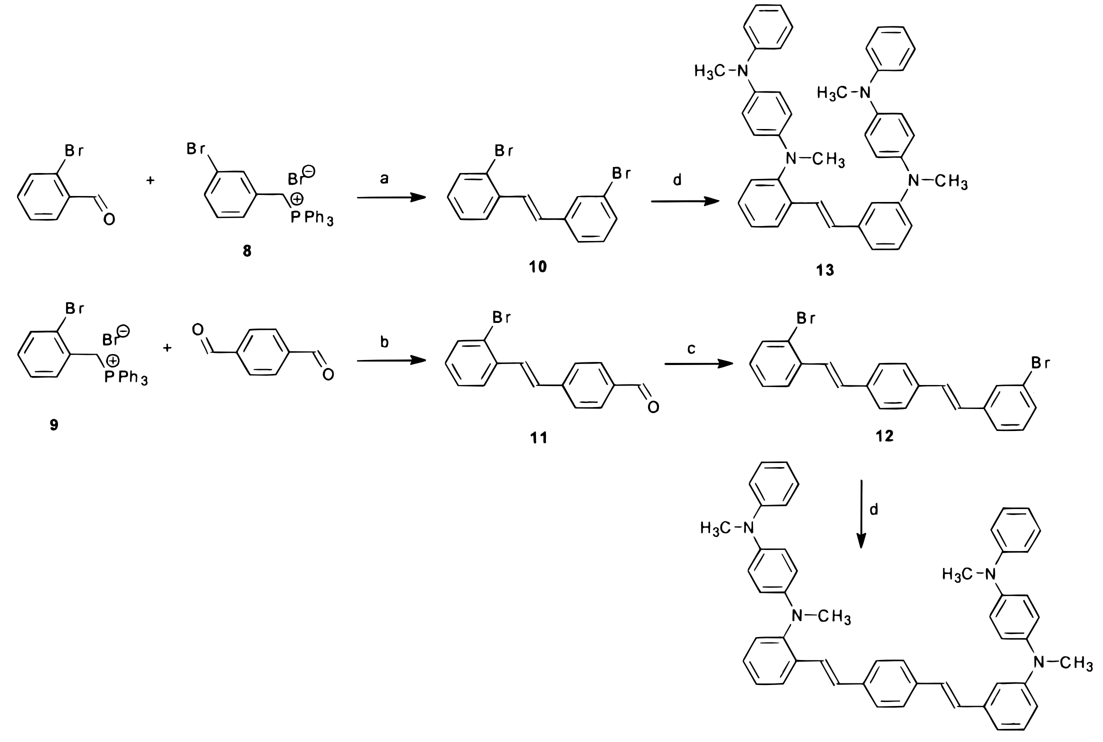
Scheme 2[a]



[a] Reagents: (a) i: BuLi, ii; I_2; (b) BuLi; (c) i: BuLi, compound **8**, ii: I_2; (d) $Pd_2(dba)_3$, DDPFA, NaO*t*Bu, *N*,*N'*-dimethyl-*N*-phenyl-1,4-benzenediamine.

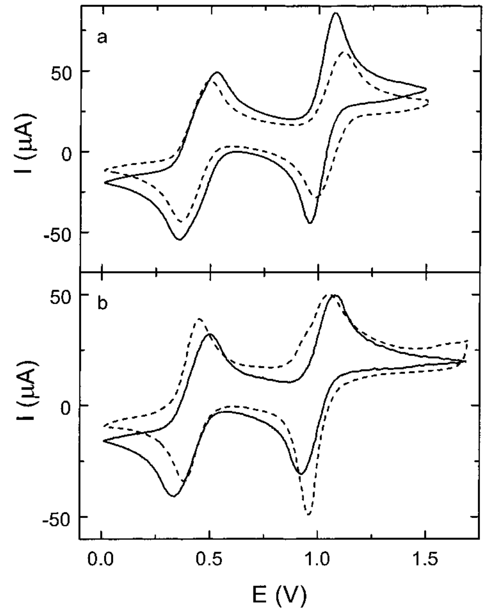


Figure 1. Cyclic voltammograms of (a) **6** (solid line) and **7** (dashed line) and (b) **13** (solid line) and **14** (dashed line), determined in $CH_2Cl_2/Bu_4{}^+NPF_6{}^-$ (0.1 mol dm^{-3}) at 295 K, scan rate 100 mV s^{-1}, potential vs SCE calibrated using Fc/Fc^+.

Table 1. Oxidation Potentials of Model Compounds 6, 7, 13, 14, and 15[a]

	$E^0{}_1$ (V)	$E^0{}_2$ (V)
6	0.42; 0.45	1.02
7	0.42	1.01
13	0.49	1.07
14	0.44	1.05
15	0.42	1.02

[a] Determined in $CH_2Cl_2/Bu_4{}^+NPF_6{}^-$ (0.1 mol dm^{-3}) at 295 K, scan rate 100 mV s^{-1}, potential vs SCE calibrated using Fc/Fc^+.

those of *N*,*N'*-dimethyl-*N*,*N'*-diphenyl-1,4-benzenediamine (**15**) implies that at $E^0{}_1$ radical cations of the pendant *p*-phenylenediamine groups are generated and, hence, at this potential radical cations and di(radical cation)s of **6** and **7** are formed. Likewise, $E^0{}_2$ is associated with the formation of the corresponding spinless *p*-phenylenediamine dications, and thus the formation of trications and tetracations of **6** and **7**. Therefore each of the oxidation waves shown in Figure 1 corresponds to a two-electron oxidation process, and oxidation of the *p*-phenylenediamine units occurs, rather than of the conjugated backbone. For **6** the first oxidation wave is somewhat broader than for **7,** and careful inspection suggests the presence two consecutive one-electron transfers with only slightly different oxidation potentials (Table 1). The increased distance between the two *p*-phenylenediamine units of **7** in comparison with **6** explains the slightly different behavior. The cyclic voltammograms of **13** and **14** show very similar results and are likewise identified with the generation of pendant *p*-phenylenediamine radical cations in the first wave and the corresponding pendant dications in the second wave. For **14** there is an additional shoulder in the voltammogram at 0.93 V, which is tentatively ascribed to the oxidation of the oligo(*p*-phenylenevinylene) backbone.

UV/vis/near-IR Absorption Spectroscopy. Quantitative conversion of the tetraamines to the different oxidation states has been achieved by chemical oxidation using thianthrenium perchlorate,[15] and these reactions can be monitored with UV/vis/near-IR absorption spectroscopy.

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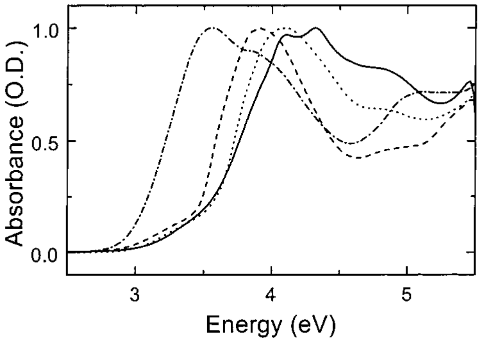

Figure 2. Normalized absorption spectra of neutral oligomers **6** (solid line), **7** (dashed line), **13** (dotted line), and **14** (dot−dashed line) recorded in dichloromethane at 295 K.

The electronic absorption spectrum of neutral **6** shows two bands at 4.12 and 4.32 eV (Figure 2). Stepwise oxidation of **6** with thianthrenium perchlorate in dichloromethane results in the gradual appearance of two new bands in the spectrum at 2.01 and 3.48 eV, associated with the formation of pendant *p*-phenylenediamine radical cations while the bands at 4.12 and 4.32 eV decrease. The new absorption bands are associated with both the radical cations ($\mathbf{6}^{\bullet+}$) and di(radical cation)s ($\mathbf{6}^{2\bullet 2+}$) of the parent oligomer (**6**). After 2 equiv were added, the bands at 2.01 and 2.38 eV reached the maximum intensity, demonstrating the near quantitative formation of the di(radical cation) ($\mathbf{6}^{2\bullet 2+}$) in which each *p*-phenylenediamine unit carries an unpaired electron. Further oxidation by addition of more than 2 equiv of thianthrenium perchlorate results in a new absorption band at 2.71 eV of doubly oxidized *p*-phenylenediamine units, i.e. trications ($\mathbf{6}^{\bullet 3+}$) and tetracations ($\mathbf{6}^{4+}$), and a simultaneous loss of the radical cation bands of $\mathbf{6}^{2\bullet 2+}$ at 2.01 and 3.48 eV (Figure 3).

As a result of the increased length of the π-conjugated oligomer, the absorption spectrum of neutral **7** at 3.91 eV has shifted to lower energy in comparison to **6** (Figure 2). Similar to **6**, oxidation of **7** results in a loss of the neutral absorption spectrum and the concomitant increase of two electronic absorptions at 2.00 and 3.50 eV, associated with radical cations ($\mathbf{7}^{\bullet+}$) and di(radical cation)s ($\mathbf{7}^{2\bullet 2+}$). Upon further oxidation these bands decrease again and are replaced by a new electronic absorption at 2.76 eV, associated with the formation of trications ($\mathbf{7}^{\bullet 3+}$) and tetracations ($\mathbf{7}^{4+}$) (Figure 3).

The absorption maximum of neutral **13** at 4.07 eV is at lower energy than the absorption of neutral **6** (Figure 2). This indicates an enhanced π-conjugation of the *p*-phenylenevinylene backbone in comparison with the *p*-phenyleneethynylene backbone. In a similar fashion as for **6** and **7**, stepwise oxidation of **13** with thianthrenium perchlorate results in two new absorption bands in the spectrum at 2.02 and 3.41 eV, indicative of the formation of the radical cations ($\mathbf{13}^{\bullet+}$) and di(radical cations) ($\mathbf{13}^{2\bullet 2+}$) (Figure 4). These bands reach a maximum intensity after addition of exactly 2 equiv and then decrease with further oxidation to make place for a new band at 2.70 eV of trications ($\mathbf{13}^{\bullet 3+}$) and tetracations ($\mathbf{13}^{4+}$). Compared to **13**, the absorption bands of neutral **14** at 3.56 and 3.90 eV are shifted to lower energy because of the increased π-conjugation (Figure 2). Compared to **6** and **7** there is a larger shift to lower energy in going from **13** to **14**, indicating a more pronounced increase of conjugation length with size for the vinylene oligomers. Upon oxidation of **14**, two absorption bands appear at 2.02 and 3.51 eV and the neutral bands are decreasing, which can be ascribed to formation of *p*-phenylenediamine radical cations $\mathbf{14}^{\bullet+}$ and $\mathbf{14}^{2\bullet 2+}$ (Figure 4). Addition of more than 2 equiv of thiantrenium perchlorate to **14** gives rise to a new absorption band at 2.70 eV of $\mathbf{14}^{\bullet 3+}$ and $\mathbf{14}^{4+}$ as in the case of **13** (Figure 4).

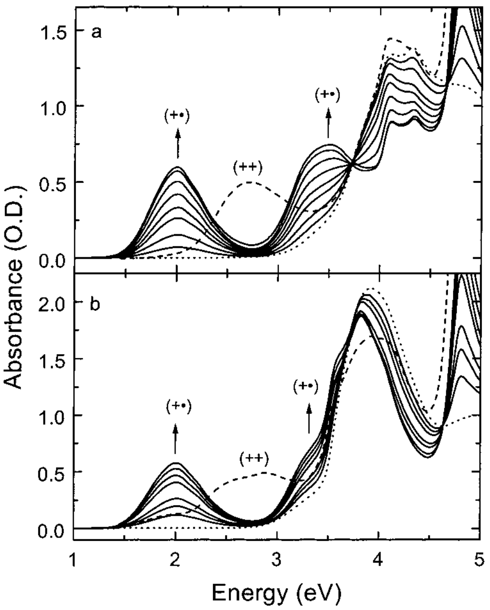

Figure 3. (a) UV/vis/near-IR spectra of **6** oxidized stepwise to $\mathbf{6}^{2\bullet 2+}$. The dotted line is the absorption of neutral **6**; the dashed line is of $\mathbf{6}^{4+}$. (b) UV/vis/near-IR spectra of **7** oxidized stepwise to $\mathbf{7}^{2\bullet 2+}$. The dotted line is the absorption of neutral **7**; the dashed line is of $\mathbf{7}^{4+}$. The symbols (+•) and (++) indicate the transitions of the pendant *p*-phenylenediamine radical cations and dications, respectively.

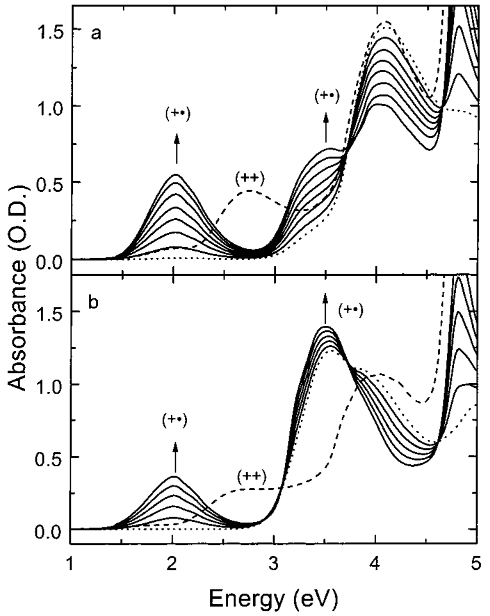

Figure 4. (a) UV/vis/near-IR spectra of **13** oxidized stepwise to $\mathbf{13}^{2\bullet 2+}$. The dotted line is the absorption of neutral **13**; the dashed line is of $\mathbf{13}^{4+}$. (b) UV/vis/near-IR spectra of **14** oxidized stepwise to $\mathbf{14}^{2\bullet 2+}$. The dotted line is the absorption of neutral **14**; the dashed line is of $\mathbf{14}^{4+}$. The symbols (+•) and (++) indicate the transitions of the pendant *p*-phenylenediamine radical cations and dications, respectively.

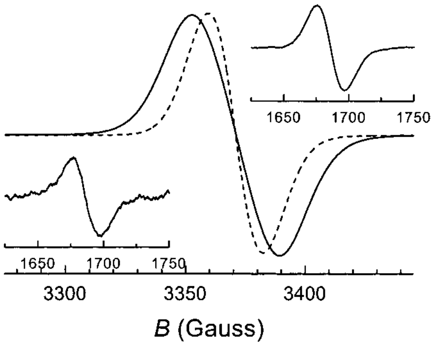

Figure 5. ESR spectra of $\mathbf{6}^{2\bullet 2+}$ (solid line) and $\mathbf{7}^{2\bullet 2+}$ (dashed line) recorded in butyronitrile at 4 K. The upper inset represents the $\Delta M_s = \pm 2$ spectrum of $\mathbf{6}^{2\bullet 2+}$ and the lower inset the $\Delta M_s = \pm 2$ spectrum of $\mathbf{7}^{2\bullet 2+}$.

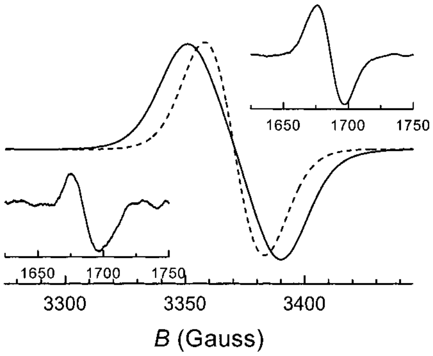

Figure 6. ESR spectra of $\mathbf{13}^{2\bullet 2+}$ (solid line) and $\mathbf{14}^{2\bullet 2+}$ (dashed line) recorded in butyronitrile at 4 K. The upper inset represents the $\Delta M_s = \pm 2$ spectrum of $\mathbf{13}^{2\bullet 2+}$ and the lower inset the $\Delta M_s = \pm 2$ spectrum of $\mathbf{14}^{2\bullet 2+}$.

These chemical oxidation experiments show that for all four compounds it is possible to carefully tune the oxidation level by addition of thiantrenium perchlorate as the oxidizing agent. In this way it is possible to selectively achieve a state in which both *p*-phenylenediamine units of **6**, **7**, **13**, and **14** are oxidized to the cation radical. The close correspondence between the electronic spectra of $\mathbf{6}^{2\bullet 2+}$, $\mathbf{7}^{2\bullet 2+}$, $\mathbf{13}^{2\bullet 2+}$, and $\mathbf{14}^{2\bullet 2+}$ demonstrates the localized nature of the radical cation in the *p*-phenylenediamine unit.

ESR Spectroscopy. The ESR spectrum of $\mathbf{6}^{2\bullet 2+}$ recorded at 4 K shows a broad signal with a width of ~37.5 G in the $\Delta M_s = \pm 1$ region and a $\Delta M_s = \pm 2$ transition at half field, characteristic of a triplet state (Figure 5). The ESR spectrum of $\mathbf{7}^{2\bullet 2+}$ recorded under similar conditions is much narrower, with a width of ~23.5 G, but also shows a $\Delta M_s = \pm 2$ transition associated with a triplet state. Despite the lack of fine structure in the $\Delta M_s = \pm 1$ region of $\mathbf{6}^{2\bullet 2+}$ and $\mathbf{7}^{2\bullet 2+}$, it is possible to estimate the zero-field parameters *D* and *E* by spectral simulation. For the simulation we first measured the ESR spectrum of the *N*,*N*'-dimethyl-*N*,*N*'-diphenyl-1,4-benzenediamine radical cation ($\mathbf{15}^{\bullet +}$) under the same conditions to obtain the intrinsic line width (~20 G) of the pendant radicals. Using this line width it is then possible to simulate the ESR spectrum of the triplet states of $\mathbf{6}^{2\bullet 2+}$ and $\mathbf{7}^{2\bullet 2+}$. We find that the ESR spectrum of $\mathbf{6}^{2\bullet 2+}$ is consistent with $D = 70 \pm 5$ MHz and $E \approx 0$ MHz, while for $\mathbf{7}^{2\bullet 2+}$ $D \leq 30$ MHz and $E \approx 0$ MHz. Given that only a single peak is observed in the ESR spectra, it must be noted that these estimates are quite limited in precision due to lack of experimental resolution. The relatively low *D* values are a direct result of the large distance between the radical centers, and the narrowing of the ESR spectrum for $\mathbf{7}^{2\bullet 2+}$ with respect to $\mathbf{6}^{2\bullet 2+}$ is consistent with the extension of the molecule. Within the magnetic dipole−dipole approximation the distance between the radical centers is related to the dipolar coupling via $D = 78000 \times d^{-3}$. Using the *D*-value estimates for $\mathbf{6}^{2\bullet 2+}$ and $\mathbf{7}^{2\bullet 2+}$ of 70 and ≤30 MHz, this suggests $d = \sim 10$ Å and $d \geq 14$ Å, respectively, as the distances between the radical centers in the two di(radical cation)s. These distances are consistent with values of ~12 Å and $d \geq 14$ Å between the centers of the two *p*-phenylenediamine rings estimated from molecular modeling assuming an anti orientation.

The ESR spectra of $\mathbf{13}^{2\bullet 2+}$ and $\mathbf{14}^{2\bullet 2+}$ recorded at 4 K show similar signals in the $\Delta M_s = \pm 1$ region with a width of ~43.5 and ~19.1 G, respectively. In addition both di(radical cation)s show a $\Delta M_s = \pm 2$ transition at half field, characteristic of a triplet state (Figure 6). The narrowing of the signal in $\mathbf{14}^{2\bullet 2+}$ in comparison with $\mathbf{13}^{2\bullet 2+}$ can be ascribed, as in the case of $\mathbf{7}^{2\bullet 2+}$, to the elongation of the molecule and the concomitant decrease of the dipolar spin−spin coupling. In the ESR spectra of $\mathbf{13}^{2\bullet 2+}$ and $\mathbf{14}^{2\bullet 2+}$ there is, again, no fine structure present in the $\Delta M_s = \pm 1$ region, but likewise it is possible to estimate the zero-field parameters *D* and *E* by spectral simulation even though the accuracy will be limited. For $\mathbf{13}^{2\bullet 2+}$ it is found that the spectrum is consistent with $D = 80 \pm 5$ MHz and $E \approx 0$ MHz, while for $\mathbf{14}^{2\bullet 2+}$ $D \leq 20$ MHz and $E \approx 0$ MHz was found. As in the case of **6** and **7**, the low zero-field splitting can be ascribed to the large distance between the radical centers. The lower *D* value for **14** with respect to **13** is consistent with the extension of the molecule. From the relation $D = 78000 \times d^{-3}$ it is possible to estimate the distance between the radical centers. For $\mathbf{13}^{2\bullet 2+}$ this yields $d = \sim 10$ Å and for $\mathbf{14}^{2\bullet 2+}$ $d \geq \sim 16$ Å. When the pendant radicals are in an anti conformation, molecular modeling gives ~12 Å and ~17 Å, for **13** and **14**, respectively, in fair agreement with these experimental estimates. The low-intensity $\Delta M_s = \pm 2$ signal for $\mathbf{14}^{2\bullet 2+}$ is consistent the low *D* value of this di(radical cation) since the theoretical ratio of the $\Delta M_s = \pm 1$ and ±2 transitions is $1{:}(D/B_0)^2$, or $1{:}4 \times 10^{-6}$ under the present conditions.[16]

Determination of the Ground States. Temperature-dependent ESR experiments show a linear relation for the doubly integrated ESR intensity (*I*) of the $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ signals of both $\mathbf{6}^{2\bullet 2+}$ and $\mathbf{7}^{2\bullet 2+}$ as a function of the reciprocal temperature between 4 and 100 K, consistent with Curie's law ($I \sim 1/T$) (Figure 7a). Similar temperature-dependent ESR results were obtained for $\mathbf{13}^{2\bullet 2+}$ and $\mathbf{14}^{2\bullet 2+}$ (Figure 7b); however, the $\Delta M_s = \pm 2$ signal of $\mathbf{14}^{2\bullet 2+}$ could only be measured between 4 and 60 K. Apparently, no population or depopulation of the high-spin states occurs in these temperature regions. This behavior is consistent with a triplet ground-state diradical with a large triplet−singlet energy gap but also with a degeneracy of singlet and triplet states for $\mathbf{6}^{2\bullet 2+}$, $\mathbf{7}^{2\bullet 2+}$, $\mathbf{13}^{2\bullet 2+}$ and $\mathbf{14}^{2\bullet 2+}$. In either case, however, the triplet state corresponds to a low-energy state.

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(16) Weismann, S. I.; Kothe, G. *J. Am. Chem. Soc.* **1975**, *97*, 2538.

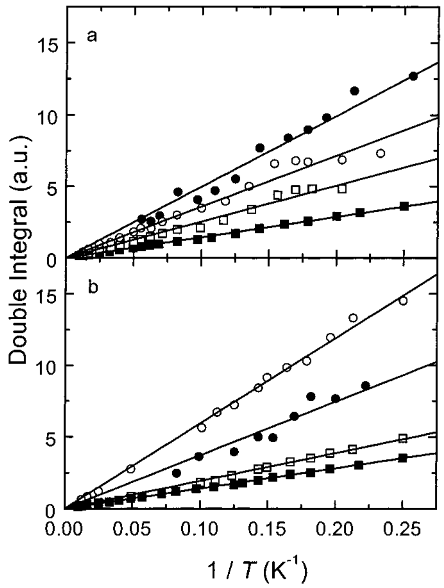

Figure 7. Temperature dependence of the ESR signal intensity of the di(radical cation)s: (a) $\mathbf{6}^{2\bullet 2+}$ (□: $\Delta M_s = ,\pm 1$; ○: $\Delta M_s = \pm 2$) and $\mathbf{7}^{2\bullet 2+}$ (■: $\Delta M_s = \pm 1$; ●: $\Delta M_s = \pm 2$); (b) $\mathbf{13}^{2\bullet 2+}$ (□: $\Delta M_s = \pm 1$; ○: $\Delta M_s = \pm 2$) and $\mathbf{14}^{2\bullet 2+}$ (■: $\Delta M_s = \pm 1$; ●: $\Delta M_s = \pm 2$). Solid lines are least-squares fits to Curie's law.

Conclusions

We have prepared triplet state di(radical cation)s of novel head-to-tail coupled oligo(1,4-phenyleneethynylene)s and oligo(1,4-phenylenevinylene)s carrying *N,N'*-dimethyl-*N'*-phenyl-1,4-benzenediamine pendant groups. The zero-field splitting in these pendant di(radical cation)s is reduced compared to di(radical cation)s coupled via a 1,3-phenylene unit[6] as a result of the increased separation between the radical centers. Although the magnitude of the exchange interaction could not be determined from the ESR experiments, the presence of $\Delta M_s = \pm 2$ ESR signals and their increasing intensity at lower temperature suggest that ferromagnetic coupling occurs between *p*-phenylenediamine radical cations in regioregular substituted π-conjugated chains between neighbors and possibly also between next-nearest neighbors. These results give support to view that pendant *p*-phenylenediamine radical cations, regioregularly substituted on a conjugated polymer chain, constitute a promising approach toward future stable high-spin polymers. Work is in progress for the synthesis of such appealing systems.

Experimental Section

General Methods. NMR chemical shifts are relative to TMS. Matrix-assisted laser-desorption ionization/time-of-flight (MALDI/TOF) mass spectra were recorded using α-cyano-4-hydroxycinnamic acid as a matrix. Cyclic voltammograms were recorded with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The working electrode was a platinum disk (0.2 cm^2), the counter electrode was a platinum plate (0.5 cm^2), and a saturated calomel electrode was used as reference electrode, calibrated against a Fc/Fc$^+$ couple. ESR spectra were recorded at X-band. An NMR gauss meter and frequency counter were used for field-frequency callibration. Temperature was controlled in a continuous helium flow cryostat. Saturation of the ESR signal during variable temperature experiments was avoided by using low microwave powers in a range such that signal intensity is proportional to square root of the microwave power at 4 K. For double integration spectra were baseline corrected. Powder simulations were carried out with a spin Hamiltonian incorporating the electron Zeeman term and the dipolar spin–spin coupling. The *g* value was assumed to be isotropic.

Materials. Commercial grade reagents were used without further purification. Solvents were purified, dried, and degassed following standard procedures. Thianthrenium perchlorate was prepared according to literature.[15] **Caution:** *Thianthrenium perchlorate is a shock-sensitive explosive solid that should be handled on small scale only.* *N,N'*-Dimethyl-*N*-phenyl-1,4-benzenediamine,[10] (3-bromobenzyl)triphenylphosphonium bromide (**8**),[17] (2-bromobenzyl)triphenylphosphonium bromide (**9**),[17] and *N,N'*-dimethyl-*N*-phenyl-1,4-benzenediamine (**15**)[10] were prepared as described in the literature.

1-Ethynyl-2-bromobenzene (1). 2-Bromoiodobenzene (10 mmol, 2.83 g) was dissolved in 20 mL of triethylamine. Argon was lead through the reaction mixture for 30 min. Trimethylsilylacetylene (12 mmol, 1.2 g), bis(triphenylphospine)-palladium(II) chloride (10 mol %, 200 mg), and copper(I) iodide (10 mol %, 100 mg) were added, and the reaction mixture was stirred for 3 h at room temperature. Then the reaction mixture was poured into water and extracted with dichloromethane (3×). The organic layers were washed with brine and dried over MgSO$_4$. The organic layer was evaporated in vacuo. The crude product was purified by column chromatography (SiO$_2$; heptane) yielding a colorless liquid (1.91 g, 75%). The liquid was dissolved in 20 mL of THF, and subsequently an equimolar amount of tetrabutylammonium fluoride (TBAF) was added. The reaction mixture was stirred for 1 h at room temperature after which it was poured into a saturated NH$_4$Cl solution and extracted with dichloromethane (3×). The organic layers were washed with brine and dried over MgSO$_4$. The solvent was removed in vacuo. The crude product was purified by column chromatography (SiO$_2$; heptane) yielding a yellow liquid (0.84 g, 62%): ^{1}H NMR (CDCl$_3$) δ 7.59 (dd, J = 8.1, 0.7 Hz, 1H) 7.53 (dd, J = 7.7, 1.8 Hz, 1H) 7.27 (dt, J = 8.1, 1.5 Hz, 1H) 7.20 (dt, J = 7.7, 1.8 Hz) 3.38 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 134.06, 132.42, 129.96, 126.97, 125.53, 124.24, 81.87, 81.79.

1-Ethynyl-3-bromobenzene (2) was prepared as described for 1-ethynyl-2-bromobenzene **1** but 3-bromoiodobenzene was used instead affording the title compound as a light yellow liquid (74%): ^{1}H NMR (CDCl$_3$) δ 7.64 (t, J = 1.5 Hz, 1H) 7.48 (dt, J = 8.1, 1.1 Hz, 1H) 7.42 (dt, J = 7.7, 1.5 Hz, 1H) 7.19 (t, J = 8.1 Hz, 1H) 3.12 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 134.86, 132.00, 130.68, 129.74, 124.09, 122.09, 82.02, 78.52.

2-Bromo,4'-iododiphenylacetylene (3). 1-Ethynyl-2-bromobenzene **1** (3 mmol, 0.55 g) and 1,4-diiodobenzene (6 mmol, 1.98 g) were dissolved in triethylamine (10 mL). Argon was bubbled through the reaction mixture for 30 min. Then bis(triphenylphosphine)palladium(II) chloride (10 mol %, 60 mg) and copper(I) iodide (10 mol %, 30 mg) were added to the reaction mixture. The reaction mixture was stirred for 3 h at room temperature after which it was poured into water and extracted with dichloromethane (3×). The combined organic layers were washed with brine and dried over MgSO$_4$. The solvent was removed in vacuo, affording the crude product which was purified by column chromatography (SiO$_2$; heptane) affording a white solid (0.56 g, 49%) mp: 70.7–73.2 °C. ^{1}H NMR (CDCl$_3$) δ 7.70 (dt, J = 8.4, 1.8 Hz, 2H) 7.61 (dd, J = 8.1, 1.1 Hz, 1H) 7.54 (dd, J = 7.6, 1.8 Hz, 1H) 7.30 (m, 3H) 7.19 (dt, J = 7.5, 1.8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 137.54, 133.19, 133.11, 132.48, 129.63, 127.86, 125.60, 125.01, 122.36, 94.65, 92.63, 89.34. Anal. Calcd for C$_{14}$H$_8$BrI: C, 43.90; H, 2.10. Found: C, 43.90; H, 2.24.

2,3'-Dibromodiphenylacetylene (4). 1-Ethynyl-2-bromobenzene **2** (5 mmol, 0.92 g) and 3-bromoiodobenzene (6 mmol, 1.7 g) were dissolved in triethylamine (15 mL). Argon was bubbled through the reaction mixture for 30 min. Then bis(triphenylphosphine)palladium(II) chloride (10 mol %, 100 mg) and copper(I) iodide (10 mol %, 50 mg) were added to the reaction mixture. The reaction mixture was stirred for 2 h at

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[17] Wallace, T. W.; Wardell, I.; Li, K.; Leeming, P.; Redhouse, A. D.; Challand, S. R. *J. Chem. Soc., Perkin Trans. 1* **1995**, *18*, 2293.

room temperature after which it was poured into water and extracted with dichloromethane (3×). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo affording the crude product which was purified by column chromatography (10% CH_2Cl_2 in *n*-heptane) affording a white solid (1,34 g, 80%) mp: 57.0−58.4 °C: ^{1}H NMR ($CDCl_3$) δ 7.73 (t, $J = 2.2$ Hz, 1H) 7.63 (dd, $J = 8.1$, 1.1 Hz, 1H) 7.55 (dd, $J = 7.7$, 1.5 Hz, 1H) 7.49 (m, 2H) 7.30 (dt, $J = 7.3$, 1.1 Hz, 1H) 7.23 (t, $J = 8.1$ Hz, 1H) 7.20 (dt, $J = 7.7$, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 134.31, 133.28, 132.49, 131.75, 130.22, 129.61, 129.73, 127.08, 125.70, 124.68, 122.18, 92.17, 89.18. Anal. Calcd for $C_{14}H_8Br_2$: C, 50.04; H, 2.40. Found: C, 50.35; H, 2.52.

2-Bromo,3”-dibromotriphenylenediacetylene (5). 2-Bromo,4’-iododiphenylacetylene **4** (1.0 mmol, 0.38 g) and 1-ethynyl-3-bromobenzene **2** (1.0 mmol, 0.18 g) were dissolved in triethylamine (5 mL). Argon was lead through the reaction mixture for 30 min. Then bis(triphenylphosphine)palladium-(II) chloride (10 mol %, 20 mg) and copper(I) iodide (10 mol %, 10 mg) were added, and the reaction mixture was stirred overnight at room temperature. The reaction mixture was then poured into water and extracted with dichloromethane (3×). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was then removed in vacuo, and the crude product was purified by column chromatography (10% CH_2Cl_2 in *n*-heptane) affording a pale yellow solid (0.25 g, 57%) mp: 94.9−96.7 °C. ^{1}H NMR ($CDCl_3$) δ 7.70 (t, $J = 1.8$ Hz, 1H) 7.63 (dd, $J = 8.0$, 1.1 Hz, 1H) 7.56 (m, 3H) 7.49 (m, 4H) 7.31 (dt, $J = 7.5$, 1.1 Hz, 1H) 7.23 (t, $J = 7.9$ Hz, 1H) 7.20 (dt, $J = 7.9$, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 134.31, 133.25, 132.49, 131.60, 130.14, 129.63, 127.08, 125.09, 124.97, 123.07, 122.69, 122.20, 90.28, 89.72. Anal. Calcd for $C_{22}H_{12}Br_2$: C, 60.58; H, 2.77. Found: C, 60.29; H, 2.85.

OPE2-tetraamine (6). An oven-dried Schlenk flask was charged with 2,3’-dibromodiphenylacetylene **4** (1 mmol, 0.34 g), *N,N’*-dimethyl-*N*-phenyl-1,4-benzenediamine (2 mmol, 0.43 g), sodium *tert*-butoxide (2.4 mmol, 0.23 g), tris(dibenzylideneacetone)dipalladium(0) (1 mol %, 9.2 mg), and (−)-(*R*)-*N,N’*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine (3 mol %, 18.8 mg). After purging with argon, dry toluene (2 mL) was added, and the reaction mixture was heated at 80 °C overnight. The reaction mixture was poured into water and extracted with dichloromethane (3×). The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed in vacuo affording a brown thick oil which was purified by column chromatography (50% CH_2Cl_2 in *n*-heptane) affording a pale yellow solid (0.32 g, 53%) mp: 110.5−113.6 °C. ^{1}H NMR ($CDCl_3$) δ 7.58 (dd, $J = 7.7$, 1.5 Hz, 1H) 7.37 (dt, $J = 7.7$, 1.8 Hz, 1H) 7.28 (m, 7H) 7.16 (m, 5H) 7.02−6.97 (m, 4H) 6.93 (t, $J = 1.1$ Hz, 1H) 6.88 (t, $J = 1.5$ Hz, 1H) 6.83 (dd, $J = 8.4$, 1.1 Hz, 1H) 6.74 (m, 5H) 3.41 (s, 3H) 3.33 (s, 3H) 3.27 (s, 3H) 3.23 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 151.16, 150.79, 150.05, 147.26, 145.59, 143.90,141.07, 134.89, 130.56, 130.16, 129.84, 127.69, 127.20, 125.73, 125.49, 124.83, 123.71, 123.52, 122.13, 121.41, 120.60, 119.98, 118.62, 118.51, 117.50, 116.09, 96.60, 87.92, 41.64, 41.55. Anal. Calcd for $C_{42}H_{38}N_4$: C, 84.2; H, 6.4; N, 9.4. Found; C, 83.89; H, 6.56; N, 9.19. MS calcd for $C_{42}H_{38}N_4$: 598.31. Found: 598.19.

OPE3-tetraamine (7). An oven-dried Schlenk flask was charged with 2,3”-dibromodiphenyldiacetylene **6** (0.9 mmol, 0.39 g), *N,N’*-dimethyl-*N*-phenyl-1,4-benzenediamine (2 mmol, 0.43 g), sodium *tert*-butoxide (2.4 mmol, 0.23 g), tris(dibenzylideneacetone)dipalladium(0) (1 mol %, 9.2 mg), and (−)-(*R*)-*N,N’*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]-ethylamine (3 mol %, 18.8 mg). After purging with argon, dry toluene (2 mL) was added, and the reaction mixture was heated at 80 °C for 2.5 days. The reaction mixture was poured into water and extracted with dichloromethane (3×). The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed in vacuo affording a brown thick oil which was purified by column chromatography (50% CH_2Cl_2 in *n*-heptane) affording a yellow solid (0.41 g, 65%) mp: 126.7−130.1 °C. ^{1}H NMR ($CDCl_3$) δ 7.58 (d, $J = 7.7$ Hz, 1H) 7.43 (d, $J = 8.0$ Hz, 1H) 7.39 (t, $J = 6.7$ Hz, 1H) 7.32−7.24 (m, 2H) 7.24−7.14 (m, 5H) 7.09−7.00 (m, 6H) 6.94 (td, $J = 7.4$, 1.0 Hz, 1H) 6.88 (dd, $J = 8.2$, 2.3 Hz, 1H) 6.82 (d, $J = 8.5$ Hz, 1H) 6.74 (m, 2H) 3.43 (s, 3H) 3.35 (s, 3H) 3.32 (s, 3H) 3.25 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 151.25, 150.73, 150.28, 147.07, 145.87, 143.63, 141.34, 134.91, 132.39, 132.32, 130.91, 130.20, 130.04, 129.88, 127.50, 127.06, 125.89, 125.65, 124.52, 124.11, 124.04, 123.42,121.66, 121.62, 120.39, 120.37, 118.86, 118.40, 117.75, 116.27, 95.87, 92.93, 90.47, 89.62, 41.66, 41.55. Anal. Calcd for $C_{50}H_{42}N_4$: C, 85.9; H, 6.1; N, 8.0. Found: C, 86.1; H, 5.65; N, 7.97. Mass calcd: 698.34. Found: 698.27.

1-(2-Bromophenyl)-2-(3-bromophenyl)ethene (10). To a suspension of (3-bromobenzyl)triphenylphosphonium bromide **8** (4 mmol, 2.1 g) in dry THF (30 mL) was added *n*-BuLi (4.2 mmol) at −30 °C. The reaction mixture was stirred for 5 min at −20 °C and then cooled to −30 °C. At this temperature 2-bromobenzaldehyde (4 mmol, 0.74 g) in dry THF (8 mL) was added at such a rate that the temperature did not rise above −20 °C. The reaction mixture was slowly warmed to room temperature and stirred overnight at this temperature. Then the reaction mixture was poured into water and extracted with diethyl ether (3×). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo. Addition of *n*-hexane to the resulting yellow oil gave a white precipitate, which was removed by filtration. The filtrate was concentrated in vacuo. After column chromatography with *n*-hexane a colorless oil (1.12 g, 83%) was obtained which was a mixture of cis- and trans-dibromide. The oil was refluxed in toluene in the presence of a catalytic amount of iodine overnight. The solvent was removed in vacuo, and the brown oil was chromatographed on silica with *n*-hexane affording a white solid (0.9 g, 67%) which was the *trans*-dibromide according to NMR, mp: 41.2−43.0 °C. ^{1}H NMR ($CDCl_3$) δ 7.69 (t, $J = 1.8$ Hz, 1H) 7.65 (dd, $J = 5.1$, 1.8 Hz, 1H) 7.59 (dd, $J = 8.1$, 1.5 Hz) 7.50−7.28 (m, 3H) 7.24 (t, $J = 7.7$ Hz, 1H) 7.14 (dt, $J = 7.7$, 1.5 Hz, 1H) 7.05 (d, $J = 16.1$ Hz, 1H) 6.95 (d, $J = 16.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 139.13, 136.61, 133.12, 130.84, 130.19, 129.83, 129.59, 129.17, 128.85, 127.58, 126.76, 125.41, 124.26, 122.91. Anal. Calcd for $C_{14}H_{10}Br_2$: C, 49.74; H, 2.98. Found: C, 50.28; H, 2.91.

1-(2-Bromophenyl)-2-(4-formylphenyl)ethene (11). To a suspension of (2-bromobenzyl)triphenylphosphonium bromide **9** (4 mmol, 2.1 g) in dry THF (30 mL) was added *n*-BuLi (4.2 mmol) at −30 °C. The reaction mixture was stirred for 5 min at −20 °C and then cooled to −30 °C. At this temperature terephthaldicarboxaldehyde (8 mmol, 1.1 g) in dry THF (8 mL) was added rapidly. The reaction mixture was slowly warmed to room temperature and stirred overnight at this temperature. Then the reaction mixture was poured into water and extracted with diethyl ether (3×). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo. Addition of *n*-hexane to the resulting yellow oil gave a white precipitate, which was removed by filtration. The filtrate was concentrated in vacuo. After column chromatography with 20% ethyl acetate in *n*-hexane a light yellow oil (0.92 g, 80%) was obtained which was a cis/trans mixture of the title compound. ^{1}H NMR ($CDCl_3$) δ 10.01 + 9.93 (s, 1H) 7.89 (dd, $J = 6.2$, 1.5 Hz, 1H) 7.70−7.60 (m, 3H) 7.40−7.26 (m, 2H) 7.19−7.09 (m, 2H) 6.79 (d, $J = 12.1$ Hz, 1H) 6.72 (d, $J = 12.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 191.64, 191.55, 142.98, 142.73, 137.25, 136.39, 135.64, 135.05, 133.23,132.88, 132.38, 130.82, 130.69, 130.23, 130.21, 130.03, 129.61, 129.56, 129.51, 129.21, 127.66, 127.24, 127.18, 126.89, 124.50, 123.76.

OPV3-dibromide (12). To a suspension of (3-bromobenzyl)-triphenylphosphonium bromide **8** (3 mmol, 1.53 g) in dry THF (25 mL) was added *n*-BuLi (3.2 mmol) at −30 °C. The reaction mixture was stirred for 5 min at −20 °C and then cooled to −30 °C. At this temperature aldehyde **11** (3 mmol, 0.9 g) in dry THF (6 mL) was added at such a rate that the temperature did not rise above −20 °C. The reaction mixture was slowly warmed to room temperature and stirred overnight at this temperature. Then the reaction mixture was poured into water and extracted with diethyl ether (3×). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo. Addition of *n*-hexane to the resulting yellow oil gave a white precipitate, which was removed by filtration. The filtrate was concentrated in vacuo.

After column chromatography with *n*-hexane, a colorless oil (1.06 g, 80%) was obtained which was a mixture of cis/trans isomers. The product was refluxed in toluene in the presence of a catalytic amount of iodine overnight. The solvent was removed in vacuo affording a brownish solid which was the trans-isomer according to NMR, which was used without further purification, mp: 125.4−128.5 °C. ^{1}H NMR ($CDCl_3$) δ 7.68 (m, 1H) 7.60−7.51 (m, 5H) 7.47−7.21 (m, 6H) 7.14−7.10 (m, 2H) 7.04 (d, $J = 16.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 139.47, 137.15, 137.02, 136.55, 136.35, 133.11, 130.99, 130.85, 130.44, 130.17, 129.65, 129.24, 128.85, 128.77, 128.70, 128.18, 127.71, 127.55, 127.23, 127.18, 127.03, 126.87, 126.65, 126.54, 125.20, 124.19, 122.92.

OPV2-tetraamine (13). An oven-dried Schlenk flask was charged with 1-(2-bromophenyl)-2-(3-bromophenyl)ethene **10** (2 mmol, 0.68 g), *N,N'*-dimethyl-*N*-phenyl-1,4-benzenediamine (4 mmol, 0.85 g), sodium *tert*-butoxide (4.8 mmol, 0.46 g), tris(dibenzylideneacetone)dipalladium(0) (1 mol %, 18.3 mg), and (−)-(*R*)-*N,N'*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine (3 mol %, 26.5 mg). After purging with argon, dry toluene (4 mL) was added, and the reaction mixture was heated at 80 °C for 5 days. The reaction mixture was poured into water and extracted with dichloromethane (3×). The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed in vacuo affording a brown thick oil which was purified by column chromatography (50% CH_2Cl_2 in *n*-heptane) affording a yellow wax (0.8 g, 67%): ^{1}H NMR ($CDCl_3$) δ 7.30−7.13 (m, 10H) 7.05−6.81 (m, 13H) 6.75−6.65 (m, 5H) 3.31 (s, 3H) 3.30 (s, 3H) 3.24 (s, 3H) 3.22 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 149.60, 149.27, 146.95, 144.01, 143.54, 139.52, 139.51, 135.39, 130.12, 129.24, 129.09, 128.87, 128.80, 127.97, 126.46, 126.39, 126.14, 124.92, 123.51, 123.06, 120.05, 118.50, 117.87, 117.62, 117.54, 116.48, 115.24, 114.90, 40.35. Anal. Calcd for $C_{42}H_{40}N_4$: C, 83.96; H, 6.71; N, 9.32. Found: C, 83.85; H, 7.09; N, 8.94. Mass calcd: 600.81. Found: 600.72.

OPV3-tetraamine (14). An oven-dried Schlenk flask was charged with **12** (1.5 mmol, 0.66 g), *N,N'*-dimethyl-*N*-phenyl-1,4-benzenediamine (3 mmol, 0.64 g), sodium *tert*-butoxide (3.6 mmol, 0.35 g), tris(dibenzylideneacetone)dipalladium(0) (1 mol %, 13.8 mg), and (−)-(*R*)-*N,N'*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine (3 mol %, 19.9 mg). After purging with argon, dry toluene (3 mL) was added, and the reaction mixture was heated at 80 °C for 5 days. The reaction mixture was poured into water and extracted with dichloromethane (3×). The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed in vacuo affording a brown thick oil which was purified by column chromatography (50% CH_2Cl_2 in *n*-heptane) affording a yellow solid (0.4 g, 38%) mp = 171.7−173.8 °C; ^{1}H NMR ($CDCl_3$) δ 7.47 (q, $J = 12.8$ Hz, 3H) 7.31−7.20 (m, 16H) 7.16−7.10 (m, 2H) 7.07−6.96 (m, 9H) 6.91−6.83 (m, 1H) 6.75−6.68 (m, 4H) 3.34 (s, 3H) 3.32 (s, 3H) 3.25 (s, 3H) 3.23 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 150.16, 149.94, 147.31, 147.08, 144.28, 143.84, 139.84, 138.46, 137.13, 137.07, 135.57, 129.57, 129.34, 129.22, 129.05, 128.35, 128.24, 127.15, 127.00, 126.66, 126.43, 125.09, 123.76, 123.32, 120.30, 118.78, 118.27, 117.95, 117.83, 116.54, 115.53, 115.16, 40.70, 40.61. Anal. Calcd for $C_{50}H_{46}N_4$: C, 85.43; H, 6.60; N, 7.79. Found: C, 84.84; H, 6.99; N, 7.48. Mass calcd: 702.94. Found: 702.73.

Acknowledgment. These investigations were supported by the Council for Chemical Sciences (CW) with financial aid from The Netherlands Organization for Scientific Research (NWO) together with the Technische Universiteit Eindhoven in the PIONIER program.

JO000548O