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Evaluation of the β Value of the Phenylene Ethynylene Unit by Probing the Exchange Interaction between Two Nitronyl Nitroxides

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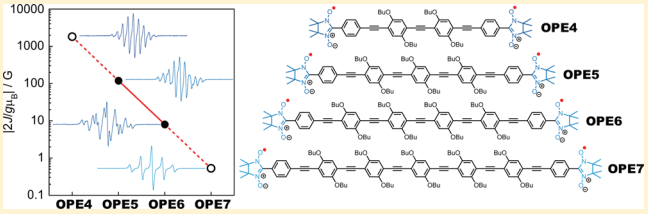
Supporting Information

ABSTRACT: A series of nitronyl nitroxide radicals having different lengths of phenylene ethynylene molecular wire were synthesized to investigate the decay constant of *p*-phenylene ethynylene. By the measurement and simulation of the ESR spectra of the biradicals, it was found that the exchange interaction decreased with a decay constant (β) of 0.39 Å^{-1} as the length of the molecule increased. This result indicates that the spin−spin exchange interaction between neutral radicals has a decay constant similar to that of the molecular conductance. This value of the decay constant indicates that a hopping mechanism does not take place in the measurement of the exchange interaction between neutral radicals even when the molecular wire has enough length to show hopping conduction of electrons.



INTRODUCTION

Molecular conductance of organic molecules is attracting interest in the field of molecular electronics because the conductance depends on the molecular geometric and electronic structure.[1−5] Tunneling and hopping mechanisms have been proposed for the origin of molecular conductance, and the tunneling mechanism is supposed to be dominant in short molecular wires.[6] Electron tunneling through the molecular wire is described with a transmission probability that decays exponentially with molecular length. The molecular conductance G is formulated in terms of the decay constant β according to eq 1:

$$G = G_0 \exp(-\beta l) \quad (1)$$

where l is the molecular length and G_0 is the contact conductance.

Oligo(*p*-phenylene ethynylene) (OPE) is a representative molecular wire that is often used in the study of molecular electronics.[6−11] The length dependence of the molecular conductance of OPE has been measured by several groups, and the decay constant β is reported to be 0.20−0.34 Å^{-1},[6,8,9] which is smaller than that of oligo(*p*-phenylene) (0.35−0.42 Å^{-1}).[12,13] Wang and co-workers also reported that when the molecular length is short enough, the conduction occurs dominantly by the tunneling mechanism, but as the molecule gets longer, the hopping mechanism starts to contribute.[6] Meanwhile, theoretical calculations of the conductance of OPE have been carried out, and the β value is reported to be 0.19−0.27 Å^{-1}, which is in good agreement with the experiment.[14,15]

The decay constants of molecular wires have been obtained not only from the direct measurement of molecular conductance but also from the rate of electron transfer[16,17] or the magnitude of the exchange interaction,[18] all of which decay exponentially with molecular length. We recently reported that the decay constant of π-conjugated wires can also be obtained by measurement[19] and calculation[20] of the exchange interaction between spins of unpaired electrons originating from organic radicals placed at the two ends of the π-conjugated wire. The reported decay constants of the exchange interaction were similar to the decay constants of the molecular conductance. Herein we report the decay constant β of OPE that was evaluated by measurement of the exchange interaction between two nitronyl nitroxide radicals. Comparison with the decay constant obtained by conductance measurements is discussed with respect to the mechanism of decay.

RESULTS AND DISCUSSION

Nitronyl nitroxide radical was used as a spin source because the radical is stable under air. Nitronyl nitroxide itself has two identical nitrogen atoms to give a five-line ESR spectrum. When two nitronyl nitroxides are magnetically coupled through an exchange interaction, the diradical gives an exchange-coupled ESR spectrum, and the value of the exchange interaction can be obtained by analyzing the splitting pattern of the spectrum.[21]

The synthesized series of molecules **OPE4**−**OPE7** are displayed in Chart 1. In order to estimate the exchange interaction, this interaction should be in the range between $|2J/g\mu_B| = 1$ G and $|2J/g\mu_B| = 300$ G because only in this region does the ESR spectrum show a splitting pattern that enables us to estimate the exchange interaction by simulation. Therefore, the number of benzene rings was set to be 4 to 7. Butoxy

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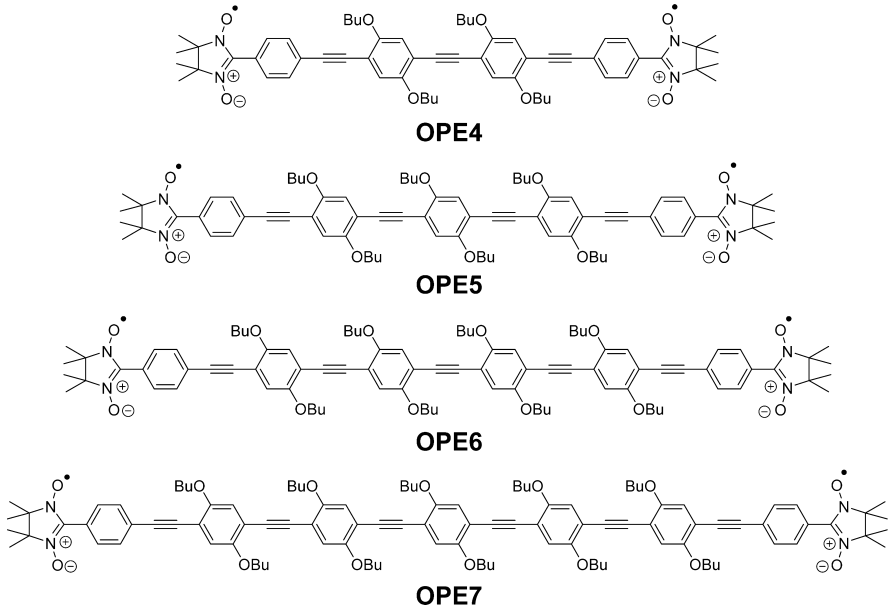
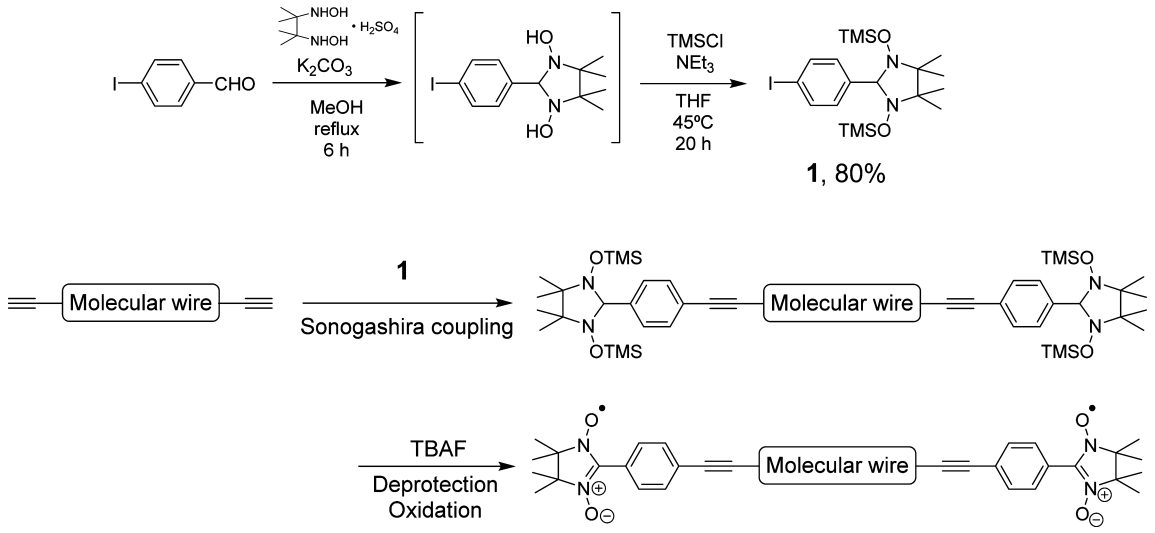
Chart 1. Synthesized Series of Bis(nitronyl nitroxide) Radicals with Different Lengths of *p*-Phenylene Ethynylene Molecular Wire



Scheme 1



groups were introduced to increase the solubility. It has been reported experimentally and theoretically that the introduction of alkoxy groups does not affect the transport of electrons.[8,22,23]

In the conventional method for preparing nitronyl nitroxides, a formyl derivative is reacted with 2,3-bis(hydroxyamino)-2,3-dimethylbutane and then the obtained cyclodehydrated derivative is oxidized to give the nitronyl nitroxide. The drawback of this method is that when several formyl groups are to be converted to nitronyl nitroxides, the yield of this step can be very low. Therefore, we adopted an alternative way to synthesize bis(nitronyl nitroxide)s. The key intermediate is iodo-substituted TMS-protected bis(hydroxylamine) **1**, which was synthesized from 4-iodobenzaldehyde in 80% yield according to the similar method reported for other silyl-protected bis(hydroxylamine)s (Scheme 1).[24,25] It was found that **1** can react with a terminal alkyne using Sonogashira coupling conditions and that deprotection using tetrabutylammonium fluoride proceeds smoothly. What is even better is that deprotection and oxidation proceed simultaneously. Therefore, simple deprotection gives the nitronyl nitroxide.

Bis(terminal alkyne)s **8**, **10**, **11**, and **13** were synthesized starting from 1,4-dibutoxy-2,5-diiodobenzene (**2**) and trimethylsilylacetylene (Scheme 2) using repetitive Sonogashira coupling and deprotection of TMS. Sonogashira coupling between bis(terminal alkyne)s and iodo-substituted TMS-protected bis(hydroxylamine) **1** afforded TMS-protected tetra(hydroxylamine)s **OPE4TMS**–**OPE7TMS** (Scheme 3). The obtained TMS-protected tetra(hydroxylamine)s were deprotected by fluoride ion and then autooxidized to give bis(nitronyl nitroxide)s **OPE4**–**OPE7**. The structures of the synthesized compounds were confirmed by NMR and ESR spectroscopy and mass spectrometry.

Phenylene ethynylene is a representative fluorescent unit that is used in functional fluorescent materials.[26] The synthesized **OPE4TMS**–**OPE7TMS** were characterized by absorption and fluorescence spectroscopy (Figure 1). As the length of the

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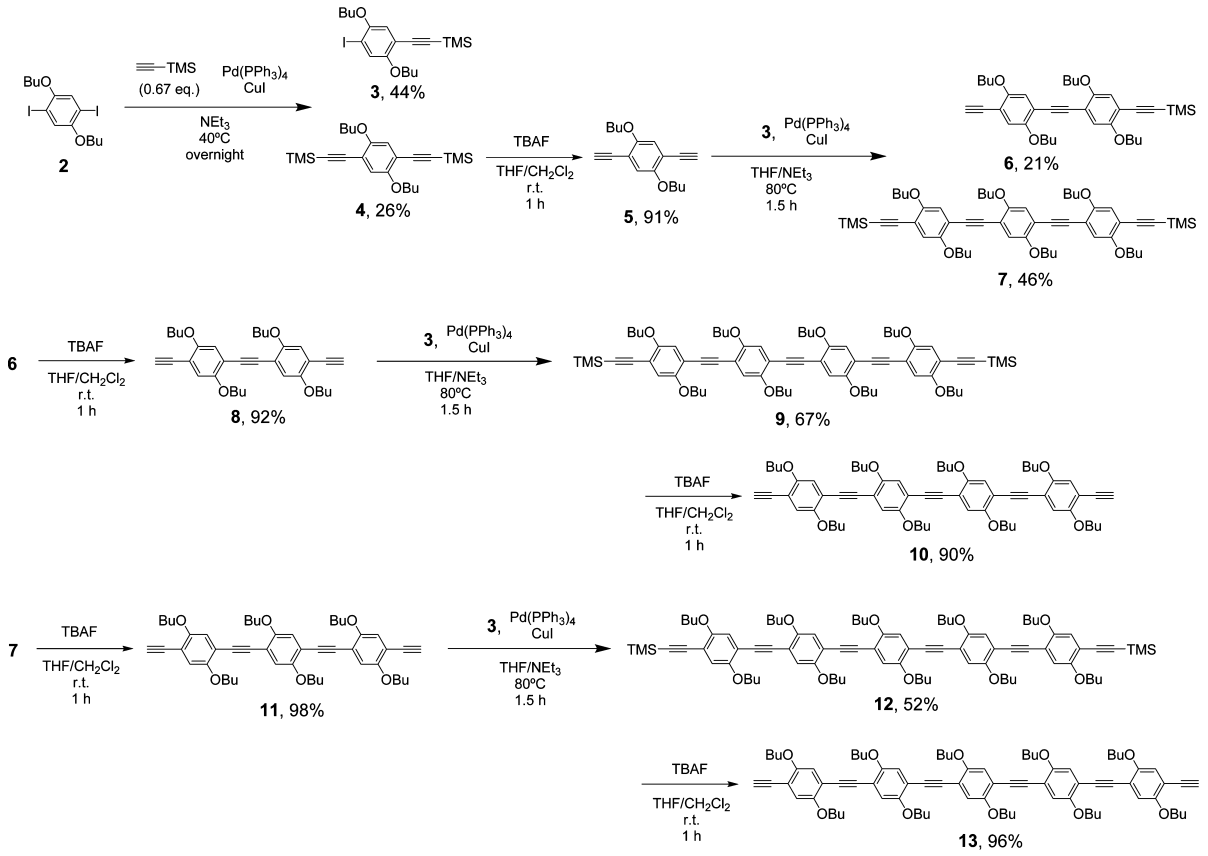
Scheme 2



molecule increased, both the absorption and fluorescence spectra showed bathochromic shifts: the absorption maximum shifted from 396 nm for **OPE4TMS** to 422 nm for **OPE7TMS**, and fluorescence maximum shifted from 435 nm for **OPE4TMS** to 469 nm for **OPE7TMS**. These results are similar to those for reported OPEs. Alkoxy substituents on the benzene ring have been reported to induce bathochromic shifts in the absorption and fluorescence spectra,[27] though no effect on the electron transport has been reported.[8,22,23]

The change in the ESR spectrum with increasing number of phenylene ethynylene moieties was examined. Figure 2 shows the ESR spectra of biradicals **OPE4**–**OPE7** measured in N_2-bubbled dichloromethane solution at room temperature. The ESR spectrum of **OPE4** shows nine lines. The ESR spectra of **OPE5** and **OPE6** show 15 lines. The exchange interaction between the two spins in **OPE5** and **OPE6** decreased with the introduction of phenylene ethynylene moieties. The biradical **OPE7** shows a five-line ESR spectrum, which means that the exchange interaction in **OPE7** is smaller than the hyperfine coupling constant.

To estimate the exchange interaction of the biradicals, the obtained spectra were simulated for several exchange interactions using the BIRADG program.[28] Biradical **OPE4** showed a nine-line spectrum, which indicates $|2J/g\mu_B| > 300$ G. From the simulation, the exchange interactions in **OPE5** and **OPE6** were determined to be $|2J/g\mu_B| = 1.2 \times 10^2$ G ($|2J/k_B| = 1.6 \times 10^{-2}$ K) and $|2J/g\mu_B| = 16$ G ($|2J/k_B| = 2.2 \times 10^{-3}$ K), respectively. Biradical **OPE7** showed a five-line spectrum, which indicates $|2J/g\mu_B| < 1$ G.

From these values of the exchange interaction, the decay constant of the phenylene ethynylene moiety was calculated (Figure 3). The value $\beta = 0.39$ Å^{-1} was obtained by assuming that the length of one phenylene ethynylene unit is 6.9 Å.[6] The J values of **OPE4** ($|2J/g\mu_B| > 300$ G) and **OPE7** ($|2J/g\mu_B| < 1$ G) could not be determined, but the obtained β value and the molecular length were consistent with the observed spectra. The reported decay constant β determined from the molecular conductance was 0.20–0.34 Å^{-1} and the reported theoretical value was 0.19–0.27 Å^{-1}, which are in good agreement with our result.

For **OPE5** and **OPE6**, when spectra for smaller J values were added to the original simulated spectra, the summed spectra reproduced the observed spectra more accurately, as shown in Figure 2i,j. This means that a certain fraction of the biradical molecules may adopt the conformation that gives the smaller exchange interaction. The spectrum of the longer wire **OPE6** was simulated using a larger amount of the additional spectrum than the spectrum of **OPE5**, suggesting that the ratio of the conformation that gives the smaller J value gets larger as the wire gets longer. Presumably, the longer wire has more possibility to adopt the conformation that gives the smaller J value.

In the measurement of the length dependence of the molecular conductance, in addition to the tunneling process, the hopping process becomes important as the molecule gets longer.[6,29] Lu et al.[6] reported that for OPE derivatives, when the molecule gets longer than three OPE units, the hopping mechanism appears and the decay constant becomes very small. The β value decreases from 0.20 to 0.03 Å^{-1} when the mechanism switches from tunneling to hopping. In this study, the observed β value was 0.39 Å^{-1}, and therefore, participation of the hopping mechanism was not observed. In the case of

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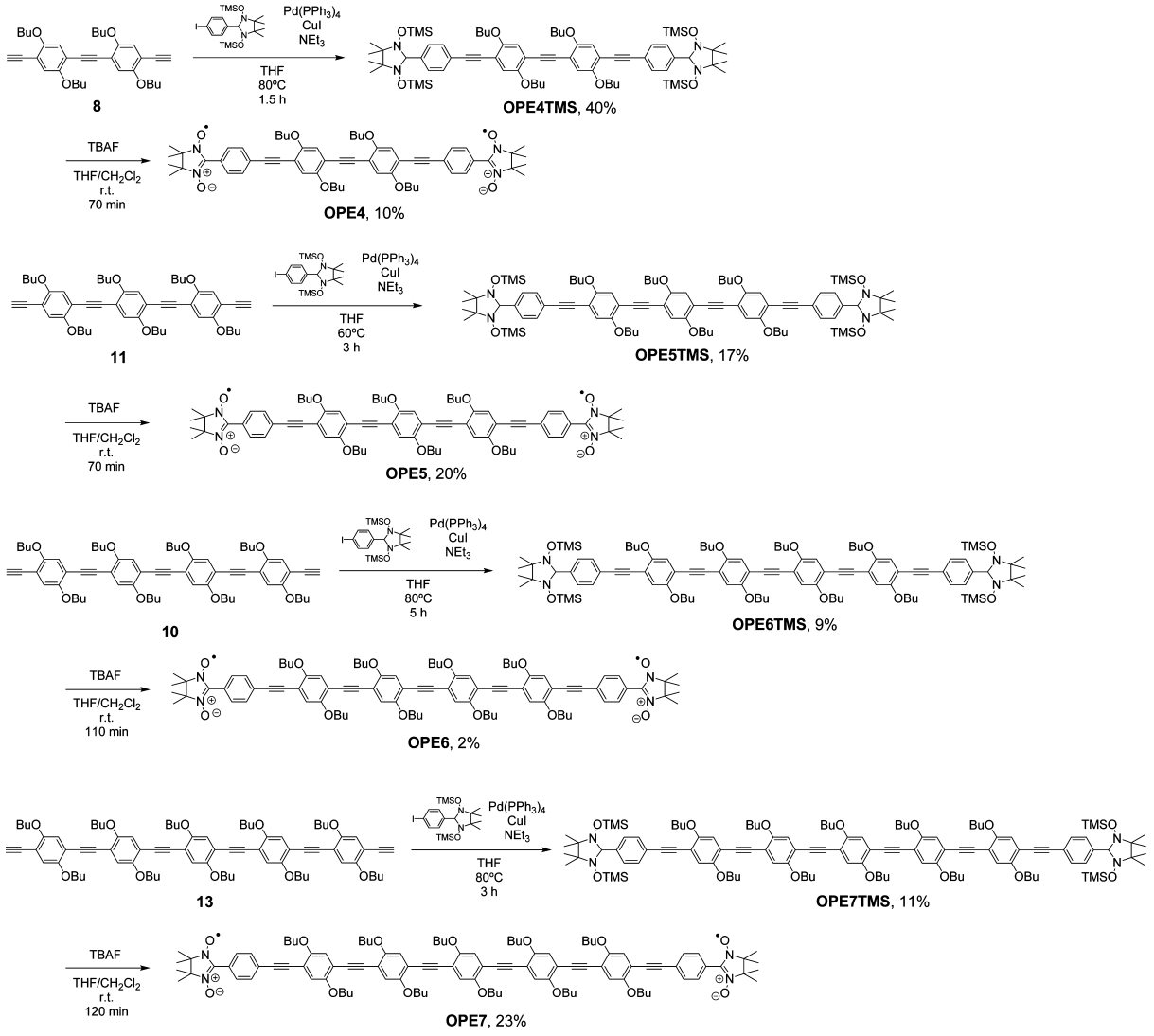
Scheme 3



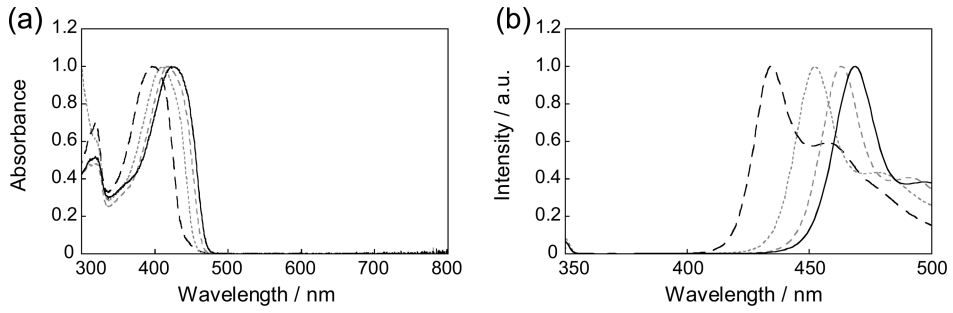


Figure 1. (a) Absorption and (b) fluorescence (λ_{ex} = 365 nm) spectra of **OPE4TMS** (black dashed lines), **OPE5TMS** (gray dotted lines), **OPE6TMS** (gray dashed lines), and **OPE7TMS** (black solid lines) measured in CH_2Cl_2. The spectra are normalized to the maximum intensity.

molecular conductance, the participation of locally charged species is responsible for the hopping mechanism, but in the case of the exchange interaction, there are no such locally charged species. Therefore, the exchange interaction reflects a pure tunneling mechanism between the two unpaired electrons.

In nitronyl nitroxide derivatives, the spin density is mainly localized in the radical substituent, and the contributions of the resonance structures are small (Scheme 4). This also supports the conclusion that our method reflects purely the electron tunneling through π-conjugation. Further theoretical and experimental investigation should provide deeper understanding of the transport phenomena through molecules.

■ CONCLUSIONS

OPE molecular wires **OPE4**–**OPE7**, which have two nitronyl nitroxide groups separated by different lengths of molecular wire, were synthesized to evaluate the decay constant (β) of the spin–spin exchange interaction (J) of the *p*-phenylene

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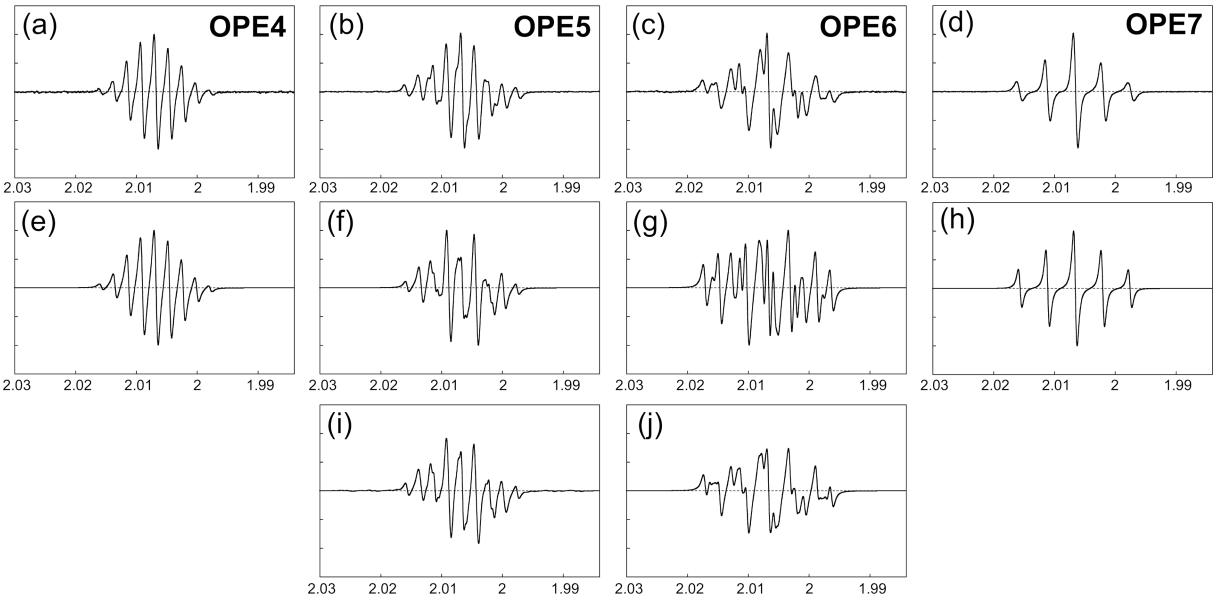


Figure 2. (a–d) X-band ESR spectra measured at room temperature for (a) **OPE4** (g = 2.0067), (b) **OPE5** (g = 2.0065), (c) **OPE6** (g = 2.0066), and (d) **OPE7** (g = 2.0065). (e–h) Simulated spectra for $|2J/g\mu_B|$ values of (e) 1800, (f) 120, (g) 8.0, and (h) 0.53 G. (i) Simulated spectrum for 80% $|2J/g\mu_B|$ = 120 G + 20% $|2J/g\mu_B|$ = 45 G. (j) Simulated spectrum for 51% $|2J/g\mu_B|$ = 8.0 G + 49% $|2J/g\mu_B|$ = 3.0 G.

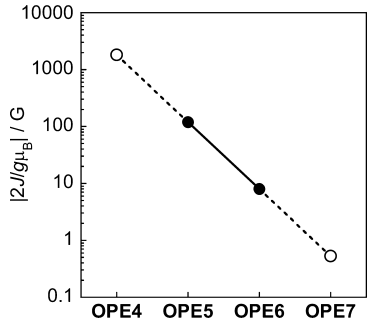


Figure 3. Correlation of the exchange interaction with the number of phenylene ethynylene moieties. The decay constant β was determined to be 0.39 Å^{-1}.

ethynylene unit. **OPE5** and **OPE6** showed complicated ESR spectra, and the values of J were determined by comparison with simulated ESR spectra. It was found that the exchange interaction decreased with the decay constant β = 0.39 Å^{-1}. This result indicates that the spin–spin exchange interaction between neutral radicals has a decay constant similar to that of the molecular conductance. The J values of **OPE4** and **OPE7** could not be determined, but the obtained β value was consistent with the observed spectra. This value of the decay constant indicates that hopping mechanism does not take place in the measurement of the exchange interaction between neutral radicals even when the molecular wire has enough length to show hopping conduction of electrons.

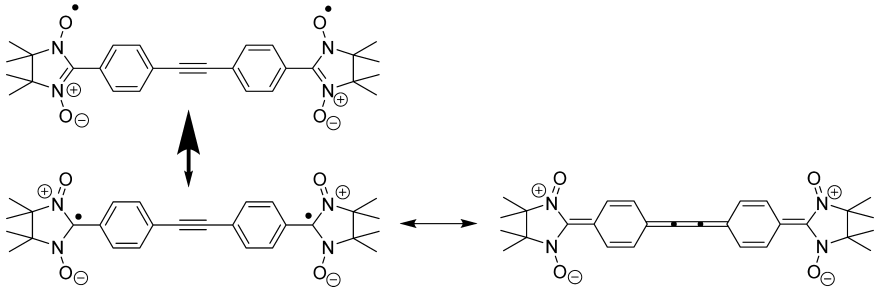
EXPERIMENTAL SECTION

1. Preparation of Materials. *General.* All of the reactions were monitored by thin-layer chromatography carried out on 0.2 mm silica gel plates. Column chromatography was performed on silica gel. Some compounds were purified by recycling preparative GPC. HPLC with a semipreparative column was used to purify biradicals **OPE4**–**OPE7**. ^{1}H and ^{13}C NMR spectra were recorded on 400, 500, and 600 MHz instruments. Samples were dissolved in $CDCl_3$, and tetramethylsilane was used as a standard. ^{13}C NMR spectra of **OPE4TMS**–**OPE7TMS** were measured at −40 °C. High-resolution mass spectra were obtained by APCI, ESI, and DART ionization using an Orbitrap analyzer.

1,4-Dibutoxy-2,5-diiodobenzene (**2**) was prepared according to the literature procedure.[30] Compounds **3**, **4**, **5**, 7, and **11** were known compounds.[31] Iodo-substituted TMS-protected bis(hydroxylamine) **1** was synthesized in a similar manner as the reported bromo-substituted derivative.[25]

1,3-Bis((trimethylsilyl)oxy)-2-(4-iodophenyl)-4,4,5,5-tetramethylimidazolidine (1). A dry methanol (100 mL) solution of 4-iodobenzaldehyde (2.3 g, 10.0 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (5.0 g, 20.0 mmol), and K_2CO_3 (2.8 g, 20.0 mmol) was refluxed for 6 h. The reaction mixture was poured into water, extracted with ethyl acetate, dried over $MgSO_4$, and

Scheme 4



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concentrated to give the bis(hydroxylamine) derivative. Purification was not performed.

To a THF (100 mL) solution of the bis(hydroxylamine) were slowly added large excesses of triethylamine (8.4 mL, 60.0 mmol) and chlorotrimethylsilane (5.2 mL, 60.0 mmol) at room temperature. After the mixture was stirred at 45 °C for 20 h, the solvent was evaporated. The residue was treated with hexane and filtered to remove the insoluble impurity. The filtrate was then concentrated. Purification with column chromatography (silica gel, hexane/CH_2Cl_2 = 60:40) gave TMS-protected bis(hydroxylamine) **1** (4.1 g, 8.0 mmol, 80%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ −0.26 (s, 18H), 1.13 (s, 6H), 1.13 (s, 6H), 4.54 (s, 1H), 7.15 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.0, 17.2, 24.5, 67.6, 92.8, 93.4, 132.3, 136.7, 141.0; ESI HRMS (m/z) [M + H]$^+$ calcd for $C_{19}H_{36}IN_2O_2Si_2$ 507.1355, found 507.1355.

*1,4-Dibutoxy-2-iodo-5-(2-(trimethylsilyl)ethynyl)benzene (**3**) and 1,4-Bis(2-(trimethylsilyl)ethynyl)-2,5-dibutoxybenzene (**4**).* A round-bottom flask was charged with 1,4-dibutoxy-2,5-diiodobenzene (**2**) (10.0 g, 0.021 mol), $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol), copper(I) iodide (0.040 g, 0.21 mmol), and NEt_3 (100 mL) and then degassed under vacuum with sonication. Trimethylsilylacetylene (3.0 mL, 0.021 mol) was then added. After 1 day of stirring at 40 °C, the mixture was concentrated, diluted with CH_2Cl_2, and then treated with 0.1 N HCl until the aqueous layer reached pH 1. The aqueous solutions were extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification with column chromatography (silica gel, hexane/CH_2Cl_2 = 90:10) gave monosubstituted **3** (4.1 g, 9.2 mmol, 44%) as a yellow oil and disubstituted **4** (1.8 g, 4.3 mmol, 26%) as a white solid.

3: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.25 (s, 9H), 0.96−0.99 (m, 6H), 1.49−1.58 (m, 4H), 1.74−1.81 (m, 4H), 3.93−3.96 (m, 4H), 6.83 (s, 1H), 7.25 (s, 1H); DART HRMS (m/z) [M + NH_4]$^+$ calcd for $C_{19}H_{33}IO_2SiN$ 462.1320, found 462.1344.

4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.25 (s, 18H), 0.98 (t, J = 7.5 Hz, 6H), 1.50−1.56 (m, 4H), 1.74−1.80 (m, 4H), 3.95 (t, J = 6.4 Hz, 4H), 6.89 (s, 2H); DART HRMS (m/z) [M + NH_4]$^+$ calcd for $C_{24}H_{42}O_2Si_2N$ 432.2749, found 432.2770.

*1,4-Dibutoxy-2,5-diethynylbenzene (**5**).* To a CH_2Cl_2 (100 mL) solution of TMS-protected alkyne **4** (0.50 g, 1.2 mmol) was added TBAF (2.8 g, 0.011 mol) in THF (ca. 20 mL) at 0 °C, and the mixture was stirred for 1 h. The reaction was quenched with brine, and the reaction mixture was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 80:20) to give alkyne **5** (0.33 g, 1.2 mmol, 98%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, J = 7.5 Hz, 6H), 1.48−1.55 (m, 4H), 1.76−1.81 (m, 4H), 3.33 (s, 2H), 3.98 (t, J = 6.5 Hz, 4H), 6.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 19.1, 31.2, 69.3, 79.7, 82.4, 113.2, 117.6, 153.9; DART HRMS (m/z) [M + NH_4]$^+$ calcd for $C_{18}H_{26}O_2N$ 288.1958, found 288.1968.

*1-(2,5-Dibutoxy-4-ethynylphenyl)-2-(2,5-dibutoxy-4-(2-(trimethylsilyl)ethynyl)phenyl)ethyne (**6**) and 1,4-Bis(2-(2,5-dibutoxy-4-(2-(trimethylsilyl)ethynyl)phenyl)ethynyl)-2,5-dibutoxybenzene (**7**).* A round-bottom flask was charged with **3** (0.75 g, 1.7 mmol), $Pd(PPh_3)_4$ (0.015 g, 0.013 mmol), copper(I) iodide (4.8 mg, 0.025 mmol), and NEt_3 (20 mL). The solution was exhaustively degassed with argon and then stirred for 30 min at 80 °C. A THF solution of alkyne **5** (0.68 g, 2.52 mmol) was then added, and then the mixture was stirred for 1.5 h. The mixture was concentrated, diluted with CH_2Cl_2, and then treated with 0.1 N HCl until the aqueous layer reached pH 1. The aqueous solution was extracted with CH_2Cl_2. All organic phases were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification with column chromatography (silica gel, hexane/CH_2Cl_2 = 90:10−40:60) gave monosubstituted **6** (0.21 g, 0.36 mmol, 21%) as a yellow oil and disubstituted **7** (0.35 g, 0.39 mmol, 46%) as a white solid.

6: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.96−1.00 (m, 12H), 1.49−1.58 (m, 8H), 1.77−1.83 (m, 8H), 3.34 (s, 1H), 3.96−4.02 (m, 8H), 6.94 (s, 1H), 6.96 (s, 1H), 6.97 (s, 1H) 6.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.1, 13.84, 13.86, 13.91, 19.16, 19.21, 19.23, 31.2, 31.32, 31.34, 31.36, 69.19, 69.23, 69.3, 69.4, 80.0, 82.3, 91.2, 91.4, 100.1, 101.1, 112.5, 113.8, 114.4, 114.9, 117.0, 117.1, 117.3, 117.9, 153.26, 153.34, 154.1, 154.2; ESI HRMS (m/z) [M + H]$^+$ calcd for $C_{37}H_{51}O_4Si$ 587.3551, found 587.3559.

7: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 18H), 0.97−1.00 (m, 18H), 1.51−1.59 (m, 12H), 1.76−1.85 (m, 12H), 3.97−4.04 (m, 12H), 6.94 (s, 2H), 6.96 (s, 2H), 6.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.1, 13.8, 13.9, 19.2, 31.4, 69.3, 69.40, 69.41, 91.4, 91.5, 100.1, 101.2, 113.8, 114.3, 114.6, 117.2, 117.3, 117.4, 153.4, 153.5, 154.2; ESI HRMS (m/z) [M + H]$^+$ calcd for $C_{56}H_{79}O_6Si_2$ 903.5410, found 903.5416.

*1,2-Bis(2,5-dibutoxy-4-ethynylphenyl)ethyne (**8**).* To a CH_2Cl_2 (10 mL) solution of partially protected alkyne **6** (0.087 g, 0.15 mmol) was added TBAF (0.17 g, 0.066 mmol) in THF (ca. 1 mL) at 0 °C, and the mixture was stirred for 1 h. The reaction was then quenched with brine, and the reaction mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 50:50) to give alkyne **8** (0.070 g, 0.14 mmol, 92%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, J = 7.5 Hz, 12H), 1.49−1.57 (m, 8H), 1.79−1.83 (m, 8H), 3.34 (s, 2H), 3.99−4.03 (m, 8H), 6.97 (s, 2H), 6.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 13.9, 19.1, 19.2, 31.2, 31.3, 69.2, 69.4, 80.0, 82.3, 91.2, 112.6, 114.8, 117.0, 117.9, 153.3, 154.1; ESI HRMS (m/z) [M + H]$^+$ calcd for $C_{34}H_{43}O_4$ 515.3156, found 515.3149.

*1,2-Bis(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-(2-(trimethylsilyl)-ethynyl)phenyl)ethynyl)phenyl)ethyne (**9**).* A round-bottom flask was charged with **3** (0.40 g, 0.90 mmol), $Pd(PPh_3)_4$ (0.035 mg, 0.030 mmol), copper(I) iodide (1.1 mg, 0.0060 mmol), and NEt_3 (20 mL). The solution was exhaustively degassed with argon. After the mixture was stirred for 30 min at 80 °C, a THF solution of alkyne **8** (0.15 g, 0.30 mmol) was added over 2 h, and then the mixture was stirred for 2 h at 80 °C. The reaction mixture was then allowed to cool to room temperature and concentrated at reduced pressure. Purification with column chromatography (silica gel, hexane/CH_2Cl_2 = 40:60) and GPC gave **9** (0.23 g, 0.20 mmol, 67%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 18H), 0.97−1.00 (m, 24H), 1.53−1.58 (m, 16H), 1.77−1.86 (m, 16H), 3.97−4.05 (m, 16H), 6.94 (s, 2H), 6.97 (s, 2H), 7.00 (s, 2H), 7.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.1, 13.85, 13.91, 19.2, 31.4, 69.2, 69.3, 91.4, 91.52, 91.56, 100.1, 101.2, 113.7, 114.2, 114.3, 114.5, 117.1, 117.2, 117.3, 153.3, 153.4, 154.2; ESI HRMS (m/z) [M + H]$^+$ calcd for $C_{72}H_{99}O_8Si_2$ 1147.6873, found 1147.6834.

*1,2-Bis(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-ethynylphenyl)-ethynyl)phenyl)ethyne (**10**).* To a CH_2Cl_2 (50 mL) solution of TMS-protected alkyne **9** (0.23 g, 0.20 mmol) was added TBAF (0.47 g, 1.8 mmol) in THF (ca. 1 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. The reaction was then quenched with brine, and the reaction mixture was extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 40:60) to give alkyne **10** (0.18 g, 0.18 mmol, 90%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97−1.01 (m, 24H), 1.48−1.63 (m, 16H), 1.78−1.87 (m, 16H), 3.35 (s, 2H), 4.00−4.06 (m, 16H), 6.98 (s, 2H), 7.00 (s, 2H), 7.01 (s, 2H), 7.01 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 13.9, 19.15, 19.22, 31.2, 31.3, 31.4, 69.26, 69.33, 69.35, 69.42, 80.0, 82.3, 91.2, 91.6, 112.5, 114.2, 114.4, 115.0, 117.0, 117.22, 117.25, 117.9, 153.3, 153.46, 153.49, 154.1; ESI HRMS (m/z) [M + H]$^+$ calcd for $C_{66}H_{83}O_8$ 1003.6082, found 1003.6072.

*1,4-Bis(2-(2,5-dibutoxy-4-ethynylphenyl)ethynyl)-2,5-dibutoxy-bezene (**11**).* To a CH_2Cl_2 (20 mL) solution of TMS-protected alkyne **7** (0.15 g, 0.17 mmol) was added TBAF (0.39 g, 1.5 mmol) in THF (ca. 2 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. The reaction was then quenched with brine, and the

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reaction mixture was extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 50:50) to give alkyne **11** (0.12 g, 0.16 mmol, 92%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97−1.00 (m, 18H), 1.51−1.58 (m, 12H), 1.79−1.85 (m, 12H), 3.34 (s, 2H), 4.00−4.05 (m, 12H), 6.98 (s, 2H), 6.99 (s, 2H), 7.00 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 13.9, 19.16, 19.22, 31.2, 31.32, 31.35, 69.2, 69.3, 69.4, 80.0, 82.3, 91.2, 91.5, 112.5, 114.2, 114.9, 117.0, 117.2, 117.9, 153.3, 153.5, 154.1; DART HRMS (m/z) $[M + H]^+$ calcd for $C_{50}H_{63}O_6$ 759.4619, found 759.4637.

*1,4-Bis(2-(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-(2-(trimethylsilyl)-ethynyl)phenyl)ethynyl)phenyl)ethynyl)-2,5-dibutoxybenzene (**12**).* A round-bottom flask was charged with **3** (0.12 g, 0.26 mmol), $Pd(PPh_3)_4$ (0.015 mg, 0.013 mmol), copper(I) iodide (0.50 mg, 0.0026 mmol), and NEt_3 (10 mL). The solution was exhaustively degassed with argon. After the mixture was stirred for 30 min at 80 °C, a THF solution of alkyne **11** (0.10 g, 0.13 mmol) was added over 1.5 h. The mixture was concentrated, diluted with CH_2Cl_2, and then treated with 0.1 N HCl until the aqueous layer reached pH 1. The aqueous solutions were extracted with CH_2Cl_2. All of the organic phases were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product. Purification with column chromatography (silica gel, hexane/CH_2Cl_2 = 20:80) gave disubstituted **12** (0.094 g, 0.068 mmol, 52%) as a yellow solid. The monosubstituted compound, 1-(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-ethynylpheny)ethynyl)phenyl)-2-(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-(2-(trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethyne, was also obtained as a yellow solid (0.038 g, 0.035 mmol, 27%).

12: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 18H), 0.97−1.01 (m, 30H), 1.52−1.60 (m, 20H), 1.77−1.87 (m, 20H), 3.97−4.06 (m, 20H), 6.94 (s, 2H), 6.97 (s, 2H), 7.00−7.01 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ −0.1, 13.85, 13.91, 19.22, 19.24, 31.4, 69.2, 69.4, 91.4, 91.5, 91.6, 100.1, 101.2, 113.7, 114.2, 114.30, 114.32, 114.6, 117.1, 117.2, 117.4, 153.3, 153.5, 154.2; ESI HRMS (m/z) $[M + H]^+$ calcd for $C_{88}H_{119}O_{10}Si_2$ 1391.8336, found 1391.8321.

Monosubstituted compound: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.97−1.01 (m, 24H), 1.50−1.60 (m, 16H), 1.77−1.87 (m, 16H), 3.35 (s, 1H), 3.97−4.05 (m, 16H), 6.94 (s, 1H), 6.97 (s, 1H), 6.98 (s, 1H), 6.99 (s, 1H), 7.01−7.00 (m, 4H); ESI HRMS (m/z) $[M + H]^+$ calcd for $C_{69}H_{91}O_8Si$ 1075.6478, found 1075.6469.

*1,4-Dibutoxy-2,5-bis(2-(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-ethynylphenyl)ethynyl)phenyl)ethynyl)benzene (**13**).* To a CH_2Cl_2 (20 mL) solution of TMS-protected alkyne **12** (0.093 g, 0.067 mmol) was added TBAF (0.16 g, 0.60 mmol) in THF (ca. 2 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature. The reaction was then quenched with brine, and the reaction mixture was extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 20:80) to afford alkyne **13** (0.080 g, 0.064 mmol, 96%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01−0.97 (m, 30H), 1.50−1.58 (m, 20H), 1.78−1.86 (m, 20H), 3.35 (s, 2H), 4.00−4.05 (m, 20H), 6.98 (s, 2H), 7.00 (s, 2H), 7.01−7.02 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 13.9, 19.2, 19.3, 31.27, 31.38, 31.41, 69.3, 69.41, 69.43, 69.5, 80.1, 82.3, 91.2, 91.57, 91.60, 91.63, 112.6, 114.2, 114.4, 114.5, 115.1, 117.1, 117.4, 118.1, 153.4, 153.5, 154.2; ESI HRMS (m/z) $[M + H]^+$ calcd for $C_{82}H_{103}O_{10}$ 1247.7546, found 1247.7523.

*1,2-Bis(2,5-dibutoxy-4-(2-(4-(4,4,5,5-tetramethyl-1,3-bis-((trimethylsilyl)oxy)imidazolidin-2-yl)phenyl)ethynyl)phenyl)ethyne (**OPE4TMS**).* A round-bottom flask was charged with alkyne **8** (0.070 g, 0.14 mmol), TMS-protected bis(hydroxylamine) **1** (0.21 g, 0.41 mmol), $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol), copper(I) iodide (2.6 mg, 0.014 mmol), THF (10 mL), and NEt_3 (5 mL). The solution was exhaustively degassed with argon. The mixture was stirred for 1.5 h at 80 °C and then allowed to cool to room temperature and concentrated at reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 50:50) and GPC to give **OPE4TMS** (0.070 g, 0.055 mmol, 98%) as a yellow powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ −0.25 (s, 36H), 1.001 (t, J = 7.5 Hz, 6H), 1.007 (t, J = 7.5 Hz, 6H) 1.15 (s, 24H), 1.52−1.61 (m, 8H), 1.82−1.88 (m, 8H), 4.03−4.07 (m, 8H), 4.61 (s, 2H), 7.02 (s, 2H), 7.03 (s, 2H), 7.39 (d, J = 8.3 Hz, 4H), 7.49 (d, J = 8.3 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ −0.2, 14.0, 14.1, 16.9, 19.06, 19.08, 24.6, 30.96, 30.98, 67.2, 68.5, 68.6, 85.4, 91.3, 92.7, 95.4, 112.9, 115.5, 115.8, 122.2, 130.0, 130.8, 141.8, 152.8; APCI HRMS (m/z) $[M + H]^+$ calcd for $C_{72}H_{111}N_4O_8Si_4$ 1271.7473, found 1271.7470; UV−vis (CH_2Cl_2) λ_{max} 396 nm.

*1,2-Bis(2,5-dibutoxy-4-(2-(4-(1-oxyl-3-oxide-4,4,5,5-tetramethyl-imidazolin-2-yl)phenyl)ethynyl)phenyl)ethyne (**OPE4**).* To a CH_2Cl_2 (5 mL) solution of **OPE4TMS** (0.010 g, 0.0079 mmol) was added TBAF (0.037 g, 0.14 mmol) in THF (ca. 1 mL), and the mixture was stirred for 70 min at room temperature. The reaction was then quenched with brine, and the reaction mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc = 90:10) to give biradical **OPE4** (0.8 mg, 0.82 μmol, 10%) as a dark-green solid.

ESI HRMS (m/z) $[M]^+$ calcd for $C_{60}H_{72}N_4O_8$ 976.5345, found 976.5332; ESR (CH_2Cl_2) nine lines, g = 2.0067, a_N = 3.8 G.

*1,4-Bis(2-(2,5-dibutoxy-4-(2-(4-(4,4,5,5-tetramethyl-1,3-bis-((trimethylsilyl)oxy)imidazolidin-2-yl)phenyl)ethynyl)phenyl)-ethynyl)-2,5-dibutoxybenzene (**OPE5TMS**).* A round-bottom flask was charged with alkyne **11** (0.090 g, 0.12 mmol), TMS-protected bis(hydroxylamine) **1** (0.18 g, 0.36 mmol), $Pd(PPh_3)_4$ (0.014 g, 0.012 mmol), copper(I) iodide (2.3 mg, 0.012 mmol), THF (10 mL), and NEt_3 (5 mL). The solution was exhaustively degassed with argon. The mixture was stirred for 3 h at 60 °C. The reaction mixture was then allowed to cool to room temperature and concentrated at reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 50:50) and GPC to give **OPE5TMS** (0.030 g, 0.020 mmol, 17%) as a yellow powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ −0.25 (s, 36H), 0.99−1.02 (m, 18H), 1.15 (s, 24H), 1.51−1.61 (m, 12H), 1.82−1.89 (m, 12H), 4.03−4.07 (m, 12H), 4.61 (s, 2H), 7.02 (s, 2H), 7.02 (s, 2H), 7.03 (s, 2H), 7.39 (d, J = 8.5 Hz, 4H), 7.49 (d, J = 8.5 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ −0.1, 14.0, 14.1, 17.0, 19.1, 24.6, 31.0, 67.2, 68.53, 68.58, 85.4, 91.4, 92.7, 95.4, 112.9, 113.1, 115.6, 115.8, 122.2, 130.0, 130.9, 141.8, 152.77, 152.8; APCI HRMS (m/z) $[M + H]^+$ calcd for $C_{88}H_{131}N_4O_{10}Si_4$ 1515.8937, found 1515.8935; UV−vis (CH_2Cl_2) λ_{max} 411 nm.

*1,4-Bis(2-(2,5-dibutoxy-4-(2-(4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl)ethynyl)phenyl)ethynyl)-2,5-dibutoxybenzene (**OPE5**).* To a CH_2Cl_2 (5 mL) solution of **OPE5TMS** (5.0 mg, 0.0033 mmol) was added TBAF (0.015 g, 0.059 mmol) in THF (ca. 1 mL) at 0 °C, and the mixture was stirred for 90 min at room temperature. The reaction was then quenched with brine, and the reaction mixture was extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc = 90:10) to give biradical **OPE5** (0.8 mg, 0.65 μmol, 20%) as a dark-green solid.

ESI HRMS (m/z) $[M]^+$ calcd for $C_{76}H_{92}N_4O_{10}$ 1220.6808, found 1220.6814; ESR (CH_2Cl_2) distorted nine lines, g = 2.0065.

*1,2-Bis(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-(2-(4-(4,4,5,5-tetramethyl-1,3-bis((trimethylsilyl)oxy)imidazolidin-2-yl)phenyl)ethynyl)-phenyl)ethynyl)phenyl)ethyne (**OPE6TMS**).* A round-bottom flask was charged with TMS-protected bis(hydroxylamine) **1** (0.14 g, 0.27 mmol), $Pd(PPh_3)_4$ (0.010 g, 0.0090 mmol), copper(I) iodide (0.3 mg, 0.0018 mmol), and NEt_3 (10 mL). The solution was exhaustively degassed with argon. After the mixture was stirred for 30 min at 80 °C, a THF solution of alkyne **10** (0.090 g, 0.090 mmol) was added over 5 h. The reaction mixture was then allowed to cool to room temperature and concentrated at reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 40:60) and GPC to give **OPE6TMS** (0.015 g, 0.0084 mmol, 9%) as a yellow powder.

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^{1}H NMR (500 MHz, $CDCl_3$) δ −0.25 (s, 36H), 0.99−1.02 (m, 24H), 1.15 (s, 24H), 1.53−1.63 (m, 16H), 1.82−1.89 (m, 16H), 4.04−4.07 (m, 16H), 4.61 (s, 2H), 7.02−7.03 (m, 8H), 7.39 (d, J = 8.0 Hz, 4H), 7.49 (d, J = 8.0 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ −0.2, 13.98, 14.03, 16.9, 19.0, 24.6, 31.0, 67.2, 68.5, 85.3, 91.4, 92.7, 95.4, 112.9, 113.0, 115.5, 115.8, 122.2, 130.0, 130.8, 141.8, 152.7, 152.8; APCI HRMS (m/z) $[M + H]^+$ calcd for $C_{104}H_{151}N_4O_{12}Si_4$ 1760.0400, found 1760.0419; UV−vis (CH_2Cl_2) λ_{max} 416 nm.

*1,2-Bis(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-(2-(4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl)ethynyl)phenyl)ethynyl)-phenyl)ethyne (**OPE6**).* To a CH_2Cl_2 (5 mL) solution of **OPE6TMS** (4.8 mg, 0.0027 mmol) was added TBAF (0.013 g, 0.049 mmol) in THF (ca. 1 mL) at 0 °C, and the mixture was stirred for 110 min at room temperature. The reaction was then quenched with brine, and the reaction mixture was extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc = 90:10) to give biradical **OPE6** (0.1 mg, 0.068 μmol, 2%) as a dark-green solid.

APCI HRMS (m/z) $[M + H]^+$ calcd for $C_{92}H_{113}N_4O_{12}$ 1465.8350, found 1465.8408; ESR (CH_2Cl_2) complicated 15 lines, g = 2.0066.

*1,4-Bis(2-(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-(2-(4-(4,4,5,5-tetramethyl-1,3-bis((trimethylsilyl)oxy)imidazolidin-2-yl)phenyl)ethynyl)-phenyl)ethynyl)phenyl)ethynyl)-2,5-dibutoxybenzene (**OPE7TMS**).* A round-bottom flask was charged with TMS-protected bis(hydroxylamine) **1** (0.11 g, 0.071 mmol), $Pd(PPh_3)_4$ (8.2 mg, 0.0071 mmol), copper(I) iodide (0.3 mg, 0.0014 mmol), and NEt_3 (10 mL). The solution was exhaustively degassed with argon. After the mixture was stirred for 30 min at 80 °C, a THF solution of alkyne **13** (0.088 g, 0.071 mmol) was added over 2 h. The reaction mixture was stirred 1 h at 80 °C and then allowed to cool to room temperature and concentrated at reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 20:80) and GPC to give **OPE7TMS** (0.016 g, 0.0077 mmol, 11%) as a yellow powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ −0.25 (s, 36H), 0.99−1.02 (m, 30H), 1.15 (s, 24H), 1.55−1.59 (m, 20H), 1.83−1.87 (m, 20H), 4.04−4.07 (m, 20H), 4.61 (s, 2H), 7.02 (m, 10H), 7.39 (d, J = 8.0 Hz, 4H), 7.49 (d, J = 8.5 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ −0.2, 13.98, 14.03, 16.9, 19.0, 24.6, 31.0, 67.2, 68.5, 85.3, 91.4, 92.7, 95.4, 112.9, 113.0, 115.5, 115.8, 122.2, 130.0, 130.8, 141.8, 152.7, 152.8; APCI HRMS (m/z) $[M + H]^+$ calcd for $C_{120}H_{171}N_4O_{14}Si_4$ 2004.1863, found 2004.1896; UV−vis (CH_2Cl_2) λ_{max} 422 nm.

*1,4-Bis(2-(2,5-dibutoxy-4-(2-(2,5-dibutoxy-4-(2-(4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenyl)ethynyl)phenyl)-ethynyl)phenyl)ethynyl)-2,5-dibutoxybenzene (**OPE7**).* To a CH_2Cl_2 (5 mL) solution of **OPE7TMS** (5.0 mg, 0.0025 mmol) was added TBAF (0.012 g, 0.045 mmol) in THF (ca. 1 mL) at 0 °C, and the mixture was stirred for 120 min at room temperature. The reaction was then quenched with brine, and the reaction mixture was extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc = 90:10) to give biradical **OPE7** (1.0 mg, 0.59 μmol, 23%) as a dark-green solid.

ESI HRMS (m/z) $[M]^+$ calcd for $C_{108}H_{132}N_4O_{14}$ 1708.9735, found 1708.9784; ESR (CH_2Cl_2) five lines, g = 2.0065, a_N = 7.6 G.

2. Spectroscopy. Absorption spectra were measured on a spectrophotometer. Fluorescence spectra were measured on a fluorescence spectrophotometer. The samples were dissolved in dry CH_2Cl_2. ESR spectra were measured on an X-band ESR spectrometer. The samples were dissolved in dry CH_2Cl_2 and degassed with N_2 bubbling for 10 min.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of synthesized compounds. 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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