# Ladderlike Ferromagnetic Spin Coupling Network on a π-Conjugated Pendant Polyradical

Takashi Kaneko,*,[†] Takahisa Makino,[†] Hiroshi Miyaji,[†] Masahiro Teraguchi,[†]
Toshiki Aoki,[†] Makoto Miyasaka,[‡] and Hiroyuki Nishide*,[‡]

*Contribution from the Department of Chemistry and Chemical Engineering,
Faculty of Engineering, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan, and
Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan*

Received May 16, 2002 ;  E-mail: kanetaka@gs.niigata-u.ac.jp

***Abstract:*** A poly(9,10-anthryleneethynylene)-based polyradical with two pendant stable phenoxyls in one anthracene skeleton was newly synthesized via polymerization of the corresponding bromoethynylanthracene monomer using a Pd(0) catalyst. The average molecular weight of the polymer reached $\bar{M}_n = 5 \times 10^3$ and was soluble in common organic solvents. The polyradical was prepared from the corresponding hydroxyl precursor polymer and was appropriately stable at room temperature. The ESR spectrum of the corresponding monomeric radical suggested an effectively delocalized spin density distribution on the backbone anthracene. The magnetization and the static magnetic susceptibility of the polyradical were measured using a SQUID magnetometer. The large average spin quantum number ($\bar{S} = {}^5/_2$) of the polyradical indicated that the ferromagnetic spin coupling network of the polyradical had spread throughout the π-conjugated chain and that it was considerably insensitive to spin defects.

## Introduction

Molecular magnetic materials have been extensively investigated during the past decade.[1] Synthesis of π-conjugated polyradicals is one of the most effective approach, because spin exchange coupling between electron spins through the π-conjugation system can be made relatively strong. The progress in this field is based on the synthesis of polyradicals with increasing values of the spin quantum number ($S$) in the electronic ground state.[2] The apparent $S$ values of one-dimensional linear π-conjugated polyradicals,[3,4] in particular, cross-conjugated polyradicals,[3] were sensitive to an unavoidable

spin defect that accompanied an increase in the length of the polymer chain. On the other hand, the polyradicals which consisted of a ladder structure combining calix[4]arene-type triarylmethanes had a ladderlike spin coupling network,[5] and, even if the unpaired electrons were separated by one spin defect, a strong magnetic interaction was maintained through another spin coupling pathway, and the huge magnetic moment, $S >$ 5400,[6] was attained for their cross-linking polyradical. Besides the ladder polyradical, another synthetic approach focuses on π-conjugated linear polymers bearing two pendant radicals in one monomer unit,[7−9] which themselves are one-dimensional linear π-conjugated polymers, but the connectivity of the neighboring radical units consists of a ladderlike spin coupling network. The one-dimensional linear π-conjugated polyradicals with a ladderlike spin coupling network possess some advantages over the ladder polyradicals in that the polymerization to produce linear polymers can be easy to access and can avoid the cross-linking that leads to the formation of insoluble polymer networks. We have designed a poly(9,10-anthryleneethynylene) with pendant radicals at the β-position (**1**), which has both very strong ferromagnetic coupling through the anthracene unit and moderately strong ferromagnetic coupling through the di-anthrylacetylene unit, as shown in Figure 1. We have previously

[†] Niigata University.

[‡] Waseda University.

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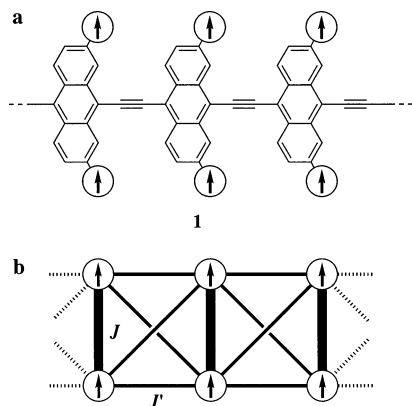
**Figure 1.** (a) Molecular structure of a poly(9,10-anthryleneethynylene) with pendant radicals at the $\beta$-position, and (b) its spin coupling pathway between neighboring radicals. *J*, very strong ferromagnetic coupling through the anthracene unit; *J'*, moderately strong ferromagnetic coupling through the dianthrylacetylene unit.
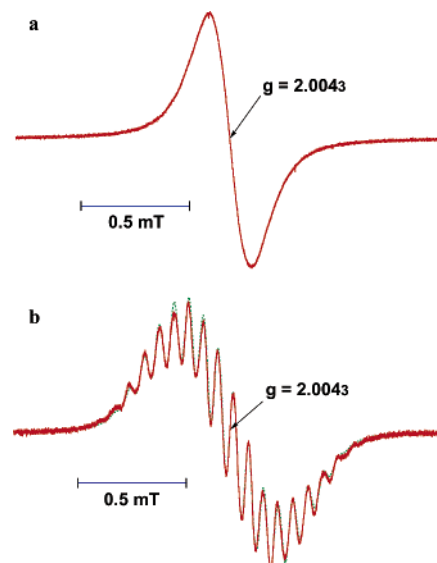
***Chart 1***
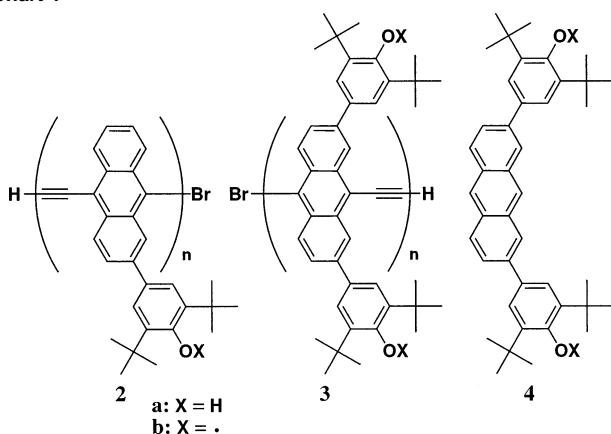


reported that the poly(9,10-anthryleneethynylene)-based polyradical **2b** causes moderately strong ferromagnetic spin coupling ($2\bar{J}' = 39 \pm 3$ cm$^{-1}$) through the $\pi$-conjugated chain.[10] In this study, we have succeeded in synthesizing the polyradical **3b** with high durability to spin defects and a larger average $S$ value as compared to that of **2b**, which corresponds to the ferromagnetic spin coupling network spreading throughout the $\pi$-conjugated chain (Chart 1).

## Results and Discussion

We newly synthesized 2,7-bis(4-acetoxy-3,5-di-*tert*-butyl-phenyl)-10-bromo-9-(3-hydroxy-3-methyl-1-butynyl)anthracene as a monomer. The polymerization of this monomer was carried out in the presence of the Pd(0) complex catalyst and the appropriate base, combining the deprotection of the ethynyl group and the cross-coupling to the aromatic halide to circumvent an oxidative coupling side reaction to produce diyne linkages.[10,11] The obtained polymer was converted to the corresponding hydroxyl polymer **3a** after complete elimination of the protecting acetyl group by treatment with alkaline solution followed by precipitation into methanol. The polymer was soluble in chloroform, tetrahydrofuran, and aromatic solvents, but insoluble in alcohols and aliphatic hydrocarbons. The

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**Figure 2.** ESR spectra of (a) the polyradical **3b** (0.5 mM, spin concentration = 0.50 spin/phenoxyl unit) in 2-methyltetrahydrofuran, and (b) 4,4′-(2,7-anthrylene)bis(2,6-di-*tert*-butylphenoxyl) (**4b**) (0.5 mM) in toluene at room temperature. The dotted line represents the simulation spectrum for **4b** using the parameters as follows: $a_H$ (mT) = 0.196 (2H), 0.155 (1H), 0.071 (4H), 0.071 (2H), 0.070 (2H), 0.050 (1H); line width 0.042 mT.

number average molecular weight and molecular weight distribution of the polymer were measured as $\bar{M}_n = 4.8 \times 10^3$ and $\bar{M}_w/\bar{M}_n = 1.5$, respectively, using GPC calibrated relative to polystyrene standards. The degree of polymerization calculated from Br analysis ($\overline{DP_n} \approx 5.7$) did not conflict with the fact that the GPC using polystyrene standards tended to overestimate the average molecular weight of poly(aryleneethynylene)s.[12]

The polyradical **3b** was obtained by oxidizing the polymer **3a** by treatment of the polymer solution in degassed 2-methyltetrahydrofuran with fresh PbO$_2$. The formation of the polyradical was supported by the appearance of the ESR signal accompanied by the decrease of the peak at 3648 cm$^{-1}$ attributed to the $\nu$O−H of the sterically hindered phenolic hydroxyl group in IR spectrum of **3a**. The structural integrity of the polyradical was also confirmed by quenching experiments of the corresponding trimer model compound (see Supporting Information). The spin concentration of **3b** was determined by doubly integrating the ESR signal in comparison with that of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) solution as a standard, and by analyzing the saturated magnetization at 2 K using a SQUID magnetometer. The spin concentration of **3b** reached ca. 0.5 spin/phenoxyl unit by selecting the oxidative conditions. The polyradical **3b** was appropriately stable for maintaining the initial spin concentration under the ESR and SQUID measurement conditions, and the half-life of the polyradical was 15 h at room temperature in the 2-methyltetrahydrofuran solution.

The ESR spectrum of **3b** shows a unimodal broad signal at $g = 2.004_3$, indicating the formation of the phenoxyl radical (Figure 2a). The spin density distribution over the anthracene unit in the polyradical is supported by the clearer hyperfine structure of the corresponding monomeric diradical, 4,4′-(2,7-anthrylene)bis(2,6-di-*tert*-butylphenoxyl) (**4b**) (Figure 2b), whose hyperfine coupling constants (mT) are estimated by spectral

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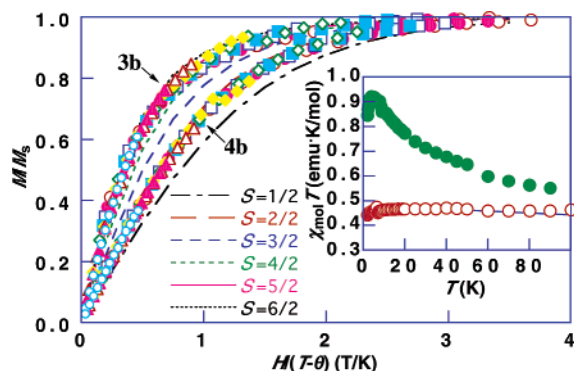
**Figure 3.** Normalized plots of magnetization ($M/M_s$) versus the ratio of magnetic field and effective temperature ($H/(T - \theta)$) for polyradical **3b** (spin concentration = 0.37 spin/phenoxyl unit) in frozen 2-methyltetrahydrofuran glass (10 mM) and monomeric diradical **4b** (spin concentration = 0.67 spin/phenoxyl unit) in frozen toluene glass (10 mM) at $T = 1.8$ (red open circle), 2 (pink filled circle), 2.25 (blue open square), 2.5 (blue filled square), 3 (green open diamond), 5 (yellow filled diamond), 7.5 (red open triangle), 10 (pink filled triangle), and 15 (blue open circle) K. Theoretical curves corresponding to $S = 1/2$, 1, $3/2$, 2, $5/2$, and 3 Brillouin functions, where $\theta$ is a weak antiferromagnetic term, were determined to be $-0.3$ (**3b**) and $-0.1$ (**4b**) K from the $\chi_{mol}T$ versus $T$ plots. Inset: $\chi_{mol}T$ versus $T$ plots of **3b** (spin concentration = 0.37 spin/phenoxyl unit) (green filled circle) and **4b** (spin concentration = 0.67 spin/phenoxyl unit) (red open circle). The solid line represents the theoretical curve calculated using the equation in ref 14 with $2J = 104$ cm$^{-1}$, $\theta = -0.10$ K, $x_1 = 0.25$, and $x_2 = 0.75$.

simulation[13] as follows: anthracene $a_H = 0.196$ (2H), 0.155 (1H), 0.071 (2H), 0.070 (2H), 0.050 (1H), phenoxyl $a_H = 0.071$ (4H). The $\Delta m_s = \pm 2$ forbidden transition was clearly observed at $g = 4$ in frozen glass at 77 K for both **3b** and **4b**.

The static magnetic susceptibility (2−100 K at 0.5 T) and magnetization (0−7 T) of **3b** were measured using a SQUID magnetometer. The sample was diluted in diamagnetic 2-methyltetrahydrofuran to minimize intermolecular interactions. The magnetization ($M$) normalized by saturated magnetization ($M_s$), $M/M_s$, of **3b** is plotted versus the ratio of magnetic field ($H$) and the effective temperature $(T - \theta)$[2c,4] and compared to the monomeric diradical **4b** and the theoretical Brillouin curves (Figure 3). Despite the spin concentration of 0.37 spin/phenoxyl unit, the plots of **3b** are located almost on the theoretical Brillouin curve of $S = 5/2$ at 1.8−15 K, while the plots of **4b** are located almost on the theoretical curve of $S = 2/2$. The $\chi_{mol}T$ versus $T$ plots of **4b** are also shown in Figure 3, where $\chi_{mol}$ is the molar paramagnetic susceptibility based on per mol of exact phenoxyl. The $\chi_{mol}T$ value of **4b** is an approximately constant value below 100 K, which was larger than the theoretical value for $S = 1/2$ ($\chi_{mol}T = 0.375$) and almost agreed with the value for $S = 2/2$ ($\chi_{mol}T = 0.5$). The $\chi_{mol}T$ value of **4b** indicates strong ferromagnetic coupling between two phenoxyls through the anthracene unit. Curve fitting of the $\chi_{mol}T$ versus $T$ data of **4b** to the modified Bleaney−Bowers relationship[14] gave $2J > 10^2$

(13) The ESR spectrum simulation was carried out with the PEST WinSim program, version 0.96 (Duling, D. R.; Laboratory of Molecular Biophysics, Public EPR Software Tools (PEST), National Institute of Environmental Health Sciences (NIEHS), 1996). Optimization of approximate parameters was carried out using the LMB1 algorithm: (a) Duling, D. R. *J. Magn. Reson., Ser. B* **1994**, *104*, 105. (b) Duling, D. R.; Motten, A. G.; Mason, R. P. *J. Magn. Reson.* **1988**, *77*, 504. As the starting set of parameters, those in ref 8 were used.

(14) The expression for the curve fitting of the $\chi_{mol}T$ versus $T$ data is $\chi_{mol}T = [N_A g^2 \mu_B^2 T/k(T - \theta)]\{x_2/[3 + \exp(-2J/kT)] + x_1/4\}$, as described in ref 4c,d, where $J$, $\theta$, $x_1$, and $x_2$ are the exchange coupling constants, the Weiss constant for a weak intermolecular magnetic interaction, and the fractions of the doublet and the triplet, respectively.

cm$^{-1}$. On the other hand, the $\chi_{mol}T$ versus $T$ plots of **3b** deviate upward from the theoretical value for $S = 2/2$ according to a decrease in temperature to reach $\chi_{mol}T = 0.92$ (corresponding to $2S = 5.4$) at 4 K, but the $\chi_{mol}T$ values are reduced below ca. 4 K. This behavior indicates a relatively strong through-bond and intrachain ferromagnetic interaction and also a weak through-space and interchain antiferromagnetic interaction probably due to the slightly aggregated chains.

## Conclusions

We have shown that the average ground-state spin quantum number of polyradical **3b** ($\bar{S} = 5/2$) became larger than that of **2b** ($\bar{S} = 2/2$)[10] at the same spin concentration, because **3b** consists of a ladderlike spin coupling network which has both the very strong ferromagnetic coupling through the anthracene unit and the moderately strong ferromagnetic coupling through the dianthrylacetylene unit. The average $S$ value of **3b** coincides with the $S$ value calculated on the assumption that the ferromagnetic spin coupling network of the polyradical has spread throughout the $\pi$-conjugated chain, considering the degree of polymerization and the spin concentration of **3b** ($\overline{DP_n} \approx 5.7$ and spin concentration = 0.37 spin/phenoxyl unit). This result indicates that this one-dimensional linear $\pi$-conjugated polyradical with the ladderlike spin coupling network is more insensitive to spin defects, although the regioregular head-to-tail $\pi$-conjugated polymers possessing pendant radicals essentially have insensitivity to spin defects due to their connectivity in that the multiple spins are connected by one ferromagnetic coupler.

## Experimental Section

**2,7-Bis(4-acetoxy-3,5-di-*tert*-butylphenyl)-10-bromo-9-(3-hydroxy-3-methyl-1-butynyl)anthracene.** The monomer, 2,7-bis(4-acetoxy-3,5-di-*tert*-butylphenyl)-10-bromo-9-(3-hydroxy-3-methyl-1-butynyl)anthracene, was synthesized from 2,7-dibromoanthracene in the same manner as the synthesis of 10-bromo-2-(3,5-di-*tert*-butyl-4-acetoxyphenyl)-9-(3-hydroxy-3-methyl-1-butynyl)anthracene as described in ref 10. The crude product was purified by silica gel column separation with chloroform and hexane/ethyl acetate (5/1 v/v) as an eluent to give the monomer. Yield 4% (from 2,7-dibromoanthracene), mp 117 °C. TLC (hexane/ethyl acetate = 5/1 v/v): $R_f = 0.23$. IR (KBr, cm$^{-1}$): 3464 ($\nu_{O-H}$), 2972−2880 ($\nu_{C-H}$, *tert*-butyl), 1768 ($\nu_{C=O}$). $^1$H NMR (CDCl$_3$, 200 MHz, ppm): $\delta$ 1.46 (s, 36H, *tert*-butyl), 1.83 (s, 6H, CH$_3$), 2.41 (s, 6H, COCH$_3$), 7.79 (s, 4H, PhH), 7.90 (dd, 2H, $J = 9.2$, 1.8 Hz, ArH), 8.62 (d, 2H, $J = 9.2$ Hz, ArH), 8.75 (d, 2H, $J = 1.8$ Hz, ArH). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 22.72, 31.51, 31.76, 35.67, 66.17, 78.69, 106.68, 117.59, 123.86, 124.44, 125.64, 127.40, 128.84, 129.28, 133.52, 137.20, 139.38, 143.09, 148.06, 171.17. Anal. Calcd for C$_{51}$H$_{59}$BrO$_5$: C, 73.63; H, 7.15; Br, 9.60. Found: C, 73.6; H, 7.1; Br, 9.6.

**Poly[2,7-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-9,10-anthryleneethynylene] (3a).** Polymerization was carried out by modifying the conditions described in ref 10. The monomer (0.25 g, 0.3 mmol), tetrakis(triphenylphosphine)palladium(0) (3.5 mg, 0.003 mmol), and copper iodide (0.57 mg, 0.003 mmol) were placed in a Schlenk tube equipped with a three-way stopcock, a reflux condenser, a rubber septum, and a Teflon-coated magnetic stirring bar. The tube was placed under vacuum, followed by a nitrogen backflush. Freshly distilled toluene (3 mL) was transferred to the tube, and the monomers were dissolved with stirring. 5 M KOH methanol solution (0.3 mL) was added to the monomer solution, and the mixture was heated at 110 °C for 3 h. After the mixture was cooled, the crude product was purified by reprecipitation from chloroform into methanol to yield the polymer as a deep blue powder. Yield 71% (calculated neglecting the end groups

of polymers). IR (KBr, cm$^{-1}$): 3652 ($\nu_{O-H}$), 2968 ($\nu_{C-H}$, *tert*-butyl), 1770 ($\nu_{C=O}$). $\bar{M}_n = 4.9 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.6$ (GPC calibrated relative to polystyrene standards).

The obtained polymer was dissolved in THF (15 mL) under a nitrogen atmosphere. DMSO (45 mL) was added to the solution, and then aqueous 2.5 M KOH (5 mL) was added to its suspension. The mixture was stirred at 50 °C for 12 h, cooled to room temperature, and neutralized with aqueous 3 N HCl. The organic product was extracted with chloroform, washed with water, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the crude product was purified by reprecipitation from chloroform into methanol to yield the polymer as a bluish black powder. Yield 88%. IR (KBr, cm$^{-1}$): 3648 ($\nu_{O-H}$), 2964−2880 ($\nu_{C-H}$, *tert*-butyl). $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 1.41 (s, 36H, *tert*-butyl), 4.3 (s, 1/$n$H, C≡C−H), 5.3 (br, 2H, OH), 7.7 (br, 4H, ArH), 7.9−8.1 (br, 2H, ArH), 8.6−9.3 (br, 4H, ArH). $\overline{DP}_n = 8$ (from $^1$H NMR). $\bar{M}_n = 4.8 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.5$ (GPC calibrated relative to polystyrene standards). Anal. Calcd for C$_{44n}$H$_{48n+1}$BrO$_{2n}$ ($n$ = 6): Br, 2.1. Found: Br, 2.3.

**Oxidation.** The monomeric diradical and polyradical were prepared by chemical oxidation of the corresponding hydroxyl precursors with PbO$_2$ under nitrogen in a glovebox as follows. A degassed toluene or 2-methyltetrahydrofuran solution of the hydroxyl precursor (0.5−10 mM per phenol unit) was treated with 10 equiv of recently prepared PbO$_2$ and was vigorously stirred for 0.5−2 h. After filtration, the solution was used for spectroscopic and magnetic measurements.

**ESR Spectroscopic Measurement.** Solutions for ESR experiments were prepared under nitrogen in a glovebox and placed in quartz tubes sealed with septa and Parafilm. ESR spectra were taken on a JEOL JES-2XG ESR spectrometer with 100 kHz field modulation in the X-band frequency region. Signal positions were calibrated against an external standard of Mn$^{2+}$/MgO ($g = 1.981$). The 77 K ESR spectra were measured for the toluene glass sample using a small Dewar flask containing the liquid nitrogen, which was inserted into the cavity of the spectrometer. The spin concentrations of each sample were determined by careful double integration of the ESR signal calibrated with that of the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) standard solution.

**Magnetic Measurement.** The solution of polyradical immediately after oxidation was used to give the sample diluted with diamagnetic toluene or 2-methyltetrahydrofuran. The sample solution was contained in a diamagnetic capsule. Magnetization and static magnetic susceptibility were measured using a Quantum Design MPMS-7 SQUID magnetometer. The magnetization was measured from 0.5 to 7 T at 1.8, 2, 2.25, 2.5, 3, 5, 7.5, 10, and 15 K. The static magnetic susceptibility was measured from 2 to 150 K in a field of 0.5 T. The spin concentrations of each sample were determined by analyzing the saturated magnetization at 2 K using a SQUID magnetometer. $M/M_s$ versus $H/(T - \theta)$ data and $\chi_{mol}T$ versus $T$ data were corrected for diamagnetism of the sample solution and the capsule, $M_{dia}$, which was determined from fitting $MT$ versus $T$ with a linear trimer model of $S = 1$ including statistical spin defects for **3b**, and with a diradical model of $S = {}^1/_2$ including monoradical contamination for **4b**. The diamagnetism from curve fitting agreed with that from the theoretical calculation using the Pascal, Gallais, and Labarre Method,[15] and the measured diamagnetism of solvent, capsule, and the composition of polyradical within the error limits to give comparable average $S$ values in $M/M_s$ versus $H/(T - \theta)$ plots.

**Other Measurements.** IR spectra were obtained using a Hitachi IR 270-30 spectrometer. NMR ($^1$H, $^{13}$C) spectra were measured using a Varian Unity 500SW (500 MHz) or a Varian Gemini 200H (200 MHz) spectrometer. Average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were evaluated by GPC using Hitachi 655A-11 Liquid Chromatograph instruments (polystyrene gel columns (Shodex KF-806L), THF eluent, polystyrene calibration).

**Supporting Information Available:** Quenching experiments of the trimer model compound (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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