A Tris(carbene) Constructed with Stable Triplet Carbene Units

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Bis[10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]diazomethane, which can generate a fairly stable triplet carbene that can survive for even a week in solution at room temperature, was shown to be stable enough to undergo a Sonogashira coupling reaction. Thus, three units of the diazo compounds were connected through an ethynyl group on 1,3,5-positions of benzene. The species generated by irradiation of the resulting tris(diazo) compound were characterized by variable temperature ESR and SQUID measurements. The results indicated the generation of the corresponding tris(carbene), that exhibits only weak exchange between carbene units. This fits the fact that dianthrylcarbenes are connected to the central phenyl ring across nodal (inactive) sites. The anomalously high thermal stability and chemical inertness of the species were shown by variable temperature and time-resolved UV–vis spectroscopic studies. The tris(carbenes) are shown to survive hours in solution at room temperature.

A great deal of work has been directed toward high-spin organic species, in which spins of unpaired electrons in 2p-orbitals of light atoms, such as carbon, nitrogen, and oxygen, are mainly used. Spin sources used for such studies are mostly thermodynamically stable radicals.[1,2] This is mainly because these radicals are usually easy to handle. One of the potential problems with these polyradicals is the weakness of the exchange coupling between the neighboring radical centers. Thus, an increased probability of thermal population in the lower-spin states cannot be avoided. Triplet carbenes are regarded as one of the most effective spin sources, since the magnitude of the exchange coupling between the neighboring centers is large.[3,4] Moreover, the photolytic production of polycarbenes is possible even in solid solution at cryogenic temperatures if poly(diazo) precursors are available. Actually, poly(diazo) compounds have been prepared, and high-spin polycarbenes have been generated.[4]

However, those systems have two disadvantages that hinder their further extension to usable magnetic materials. First, a triplet carbene unit is highly unstable and lacks stability for practical application under ambient conditions. Secondly, diazo groups are also generally labile,[5] and, hence, the diazo compound cannot be used as a building block to prepare a more complicated poly(diazo) compound.

In order to overcome these difficulties, we have made great efforts to stabilize a triplet carbene and succeeded in preparing fairly stable ones that survived for days in solution at room temperature.[6] We also found that a diphenyldiazomethane prepared to generate a persistent triplet carbene is also persistent for the diphenyldiazo compound and, hence, can be further modified, with the diazo group intact, into a more complicated diazo compound.[7–10]

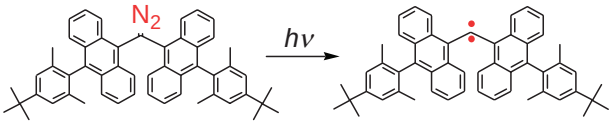
Thus, it is now potentially possible to prepare a stable polycarbene by connecting a stable carbene precursor diazo unit in a proper manner. We wish to report here that a tris(diazo) compound consisting of a dianthryl diazo compound generated a fairly stable tris(carbene).

Results and Discussion

Preparation of a Tris(diazo) Compound. The diazo unit that we used in this study was bis[10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]diazomethane (**1**-N_2), which can generate a fairly stable triplet carbene that survives even a week in solution at room temperature (Scheme 1).[11,12]

In order to attach a handle connecting this unit to a linker, we first prepared the dianthryl diazo compound (**2**-N_2), which has a bromine group at the 3 position of the anthryl ring, according to the procedures summarized in Scheme 2. Then, this diazo compound was treated with trimethylsilylacetylene in the presence of [$PdCl_2(Ph_3P)_2$] and CuI at 40 °C for 1 day. This treatment gave **3**-N_2(TMS). Deprotection[13] of the trimethylsilyl group of **3**-N_2(TMS) with NaOH proceeded smoothly to give an ethynyl derivative **3**-N_2. A desired tris(diazo) compound (**4**-$3N_2$) was then prepared by coupling three equivalents of **3**-N_2 with 1,3,5-triiodobenzene[14] under mild Sonogashira coupling reaction conditions (Scheme 3).[15]

The characterization of the tris(diazo) compound (**4**-$3N_2$) was mainly based on ^{1}H and ^{13}C NMR and IR spectra. The ^{1}H NMR spectrum of **4**-$3N_2$ showed two singlets (δ 1.46 and 1.79 ppm) corresponding to the *t*-butyl and methyl groups, respectively, and an aromatic singlet (δ 7.54 ppm) in the ratio of 18:12:1, in agreement with the calculated value. A strong and sharp band at 2048 cm^{-1} was observed in the IR spectrum. However, molecular weight determination by using MS could



1-N_2 **1**

Scheme 1.

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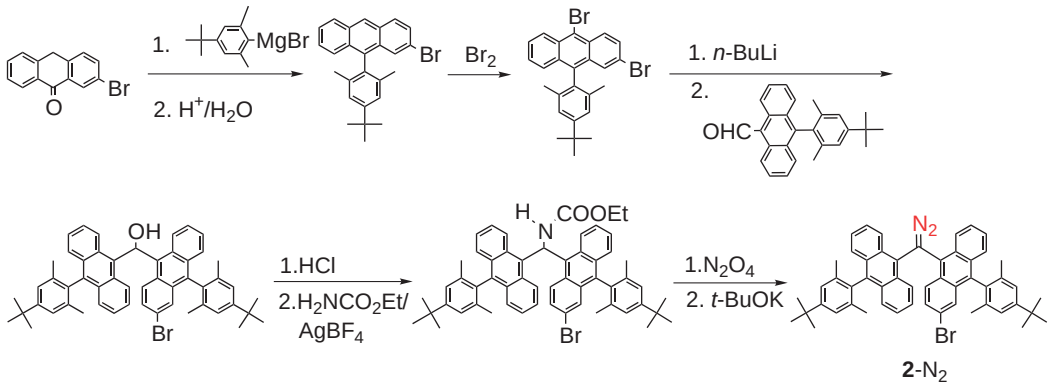
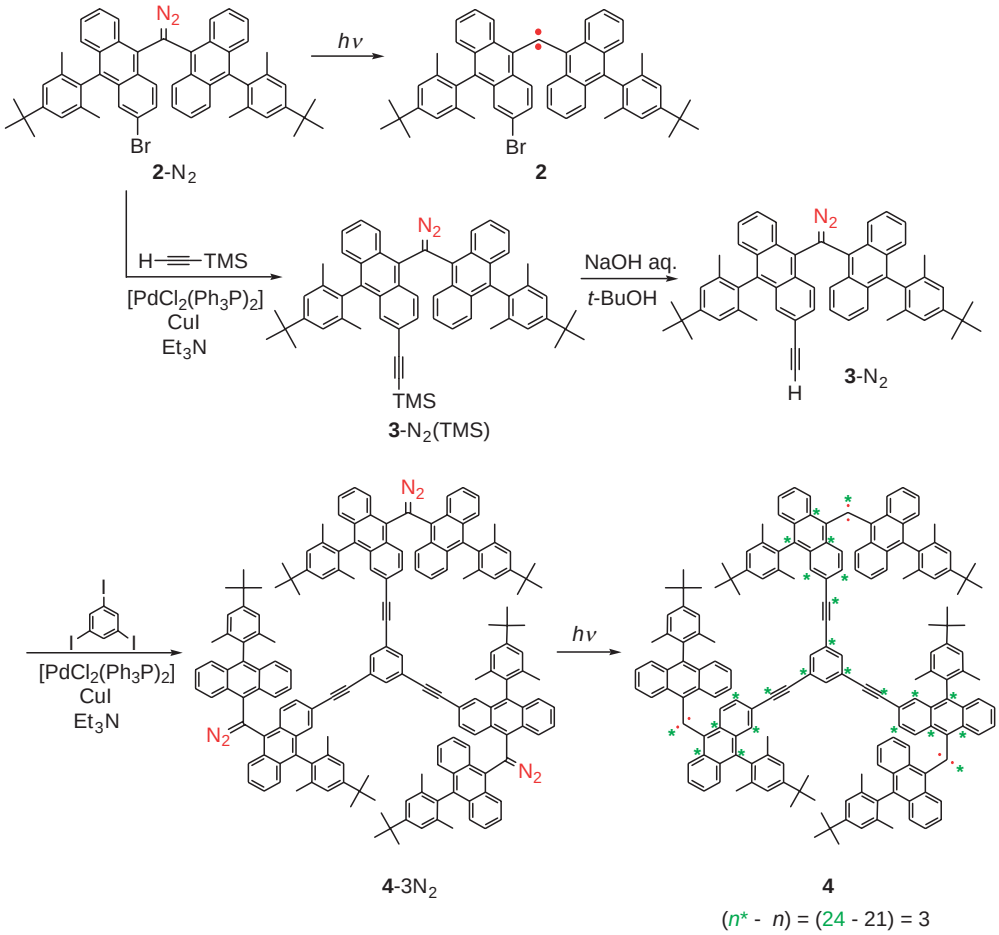


Scheme 2.

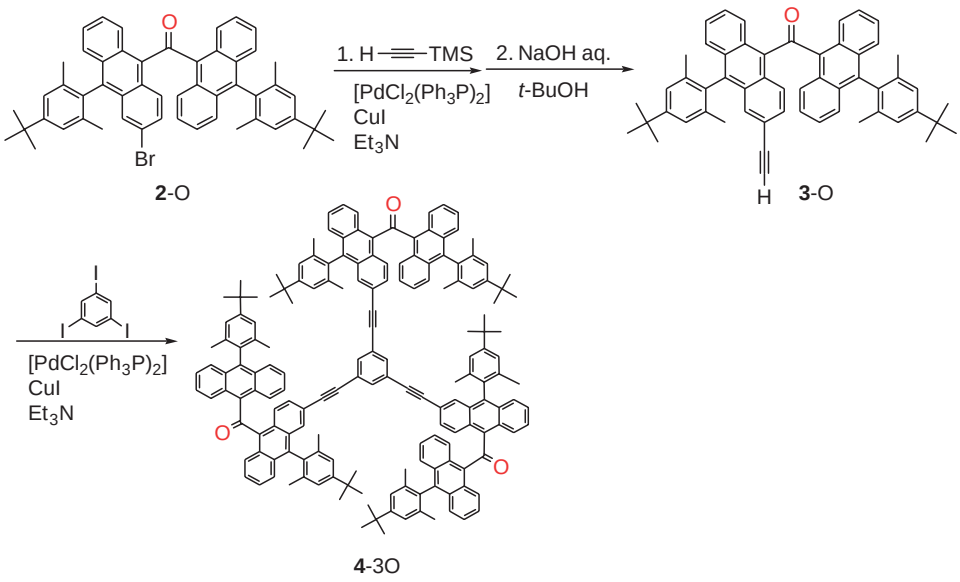


Scheme 3.

not be used in the present system since the diazo functional groups could not survive ionization processes. One idea to solve this problem is to convert all the diazo groups in **4**-3N_2 to a stable functional group and to determine the molecular weight of the resulting trimeric product. This sounded reasonable since there are several ways to quantitatively convert diazo groups to other functional groups; such methods include the treatment with hydrochloric acid to give the corresponding chloride and photolysis in methanol to give the methyl ether as a result of the O–H insertion of the photogenerated carbene into the solvent.[5,16] However, all attempts to convert **4**-3N_2 cleanly to a tris compound with a stable functional group were unsuccessful. This is obviously due to the highly congested nature of its reaction center.

Therefore, we decided to prepare an "authentic" sample. Tris(ketone) (**4**-3O) was prepared following essentially the same reaction procedure as outlined in Scheme 3 using 3-bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl 10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl ketone (**2**-O) as a starting compound (Scheme 4).

Matrix-assisted laser desorption ionization time-of-flight MS (MALDI-TOF MS) of the tris(ketone) (**4**-3O) afforded



Scheme 4.

an M^+ ion peak at 2251.1432 (1:1 $CH_3OH/CHCl_3$, positive mode). The spectrum for the M^+ ion cluster from the high-resolution spectrum exhibited isotopic distributions essentially identical with those simulated for $C_{171}H_{150}O_3$ (Fig. S1). The fully characterized tris(ketone) **4**-3O was then used as a "standard" in the analysis of the diazo counterpart by GPC. The elution volume of **4**-$3N_2$ was actually found to be in complete agreement with that of **4**-3O (Fig. S2).

ESR Studies. Irradiation ($\lambda > 350$ nm) of a mono(diazo) compound (**2**-N_2) in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave rise to a paramagnetic species (Fig. 1a) readily characterized from its ESR spectrum as a derivative of a triplet carbene (^{3}**2**).[12,17] The ESR signals were persistent at this low temperature but disappeared irreversibly when the matrix temperature was raised to room temperature and recooled to 77 K. The ESR signals were analyzed in terms of zero-field splitting (ZFS) parameters, which gave $|D| = 0.103$ cm^{-1} and $|E| = 0.0006$ cm^{-1} ($E/D = 0.0058$). These values are very similar to those ($|D| = 0.102$ cm^{-1} and $|E| = 0.0008$ cm^{-1}, $E/D = 0.0078$) observed for ^{3}**1** obtained by irradiation of **1**-N_2.[12]

In order to examine the stability of ^{3}**2**, we carried out a variable-temperature ESR study. The thermal stability of the triplet carbenes could be estimated by gradually warming the matrix containing triplet carbenes to a desired temperature; the mixture was kept at this temperature for 5 min and recooled again to 77 K to measure the signal. This procedure can compensate any weakening of signals due to the Curie law.[18] When the 2-MTHF glass containing ^{3}**2** was warmed to around 95 K, a new set of triplet peaks ($|D| = 0.088$ cm^{-1} and $|E| = 0.0003$ cm^{-1}) appeared at the expense of the original peaks (Fig. 1b). These changes were not reversible; when the sample was cooled to 77 K, no change took place, except that the signal intensity increased according to the Curie law. Changes of this kind have often been observed for sterically congested triplet diarylcarbenes and are usually interpreted in terms of the geometrical relaxation of the carbenes as the viscosity decreases upon warming.[19,20] Significant decay of the new set of signals was observed only at 280 K,

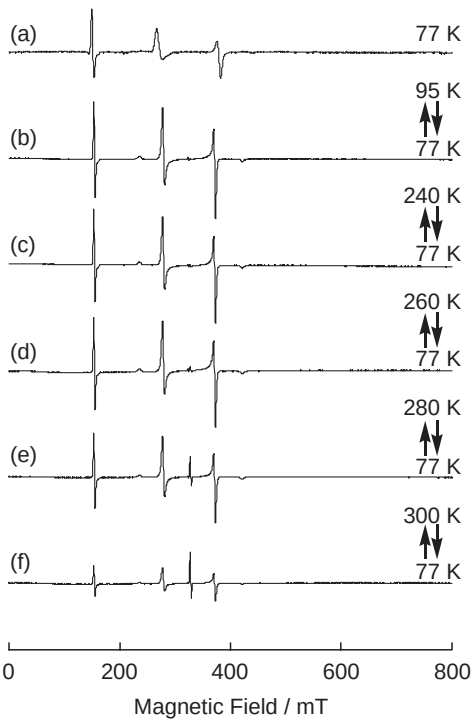


Fig. 1. (a) ESR spectrum obtained by irradiation of mono-diazo compound **2**-N_2 in 2-methyltetrahydrofuran at 77 K. (b–f) ESR spectra observed at 77 K in 2-methyltetrahydrofuran after warming the matrix containing ^{3}**2** to (b) 95, (c) 240, (d) 260, (e) 280, and (f) 300 K.

and the signals were observable even at 300 K. However, the signals disappeared completely after the sample was kept at room temperature for 15 min (the measurements were made at 77 K). This result is to be compared with that observed for ^{3}**1**, whose ESR signals were observed even after standing for three hours at room temperature.[12b] A marked decrease in the thermal stability was thus noted once a bromo substituent was introduced at 3 position.

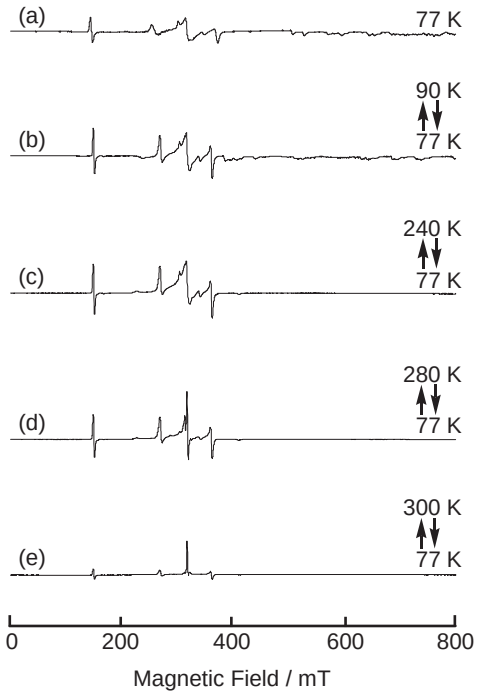


Fig. 2. (a) ESR spectrum obtained by irradiation of tris(diazo) compound **4**-$3N_2$ in 2-methyltetrahydrofuran at 77 K. (b–e) ESR spectra observed at 77 K in 2-methyltetrahydrofuran after warming the matrix containing **4** to (b) 90, (c) 240, (d) 280, and (e) 300 K.

Similar irradiation ($\lambda > 350$ nm) of the tris(diazo) compound **4**-$3N_2$ in a 2-methyltetrahydrofuran (2-MTHF) solid solution at 77 K produced ESR signals (Fig. 2). The signals at 147.9, 262.0, and 386.2 mT were similar to those observed for triplet monocarbene ^{3}**2** obtained by the photolysis of **2**-N_2 and were analyzed in terms of the zero-field splitting (ZFS) parameters ($|D| = 0.106$ cm^{-1} and $|E| = 0.0008$ cm^{-1}). However, those at 310.4 and 324.5 mT were obviously different from those of the monocarbene triplet and were attributable to a higher spin state.

In order to assign the signals, we carried out computer simulations.[21] The spectra simulated for $S = 1$ ($g = 2.003$, $|D| = 0.024$ cm^{-1}, and $|E| = 0.0003$ cm^{-1}), $S = 2$ ($g = 2.003$, $|D| = 0.009$ cm^{-1}, and $|E| = 0.000$ cm^{-1}), and $S = 3$ ($g = 2.003$, $|D| = 0.009$ cm^{-1}, and $|E| = 0.000$ cm^{-1}) indicate that there are only subtle differences among the three spectra (Fig. S3). The observed peaks can thus be fitted to either ^{1}**4** or ^{5}**4** or ^{7}**4**. Thus, we could not confidently assign the signals. The pattern of the signals did not change from the initial to the latter stages of irradiation (Fig. S6), and all signals were observable even at 4 K.

In order to identify the origin of those signals, we investigated the temperature dependency of the signal intensities. Thus, a 2-MTHF matrix containing **4**-$3N_2$ was irradiated at 4 K, and two signals (at 147.9 and 262.0 mT) due to triplet species and another two (at 310.4 and 324.5 mT) ascribable to higher-spin species were used for the study of the temperature dependence. The intensities of all the signals decreased as the temperature was raised. Reproducible signal intensities were obtained in the temperature range of 10–85 K. The plots of the signal intensities of all the signals vs the reciprocal of the temperature (Fig. 3) were linear.

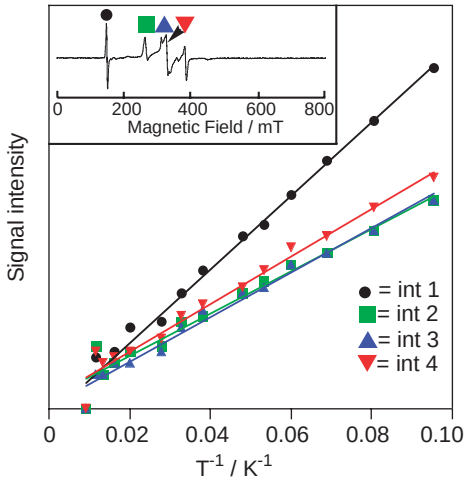


Fig. 3. Plots of the intensities of the ESR signals at 262.0 and 147.9 mT due to triplet species and at 324.5 and 310.4 mT due to a higher-spin species vs reciprocal of temperature (10–85 K).

These observations suggest that all the signals are attributable to the ground states. It is possible that triplet species originate from monocarbene (formed due to incomplete photodecomposition), while high-spin species are formed as a result of complete decomposition. Another possibility is that the four states (singlet, triplet, quintet, and septet) originate from one species, in which they are degenerate. However, the latter possibility is excluded by the variable-temperature study of ESR signals, the ZFS parameters, and the wavelength dependence of the spectrum (vide infra).

In order to examine the stability of those high-spin species, we conducted a variable-temperature ESR study. Slight but distinct shifts of the signals were observed along with an apparent increase in the intensity when the matrix was warmed to 90 K. The ZFS parameters obtained for the triplet species ($|D| = 0.086$ cm^{-1} and $|E| = 0.0006$ cm^{-1}) slightly decreased, suggesting again that the species undergo geometrical relaxation upon warming.[19,20] No significant decay of the signals was observed until the matrix temperature was raised to 280 K, and the signals were observable even at 300 K. Anomalously high thermal stability was thus noted.

SQUID Measurement. In order to obtain more information on the ground state multiplicity, we carried out magnetic measurements. The 2-MTHF solution of tris(diazo) compounds (**4**-$3N_2$) was placed inside the sample compartment of a superconducting quantum interference device (SQUID) magnet/susceptometer and irradiated at 5–10 K with light ($\lambda = 488$ nm) from an argon ion laser through an optical fiber. The development of magnetization (M/emu) at 5 K in a constant field of 5 kOe with the irradiation time for the tris(diazo) compound was measured in situ and is shown in Fig. 4a. As the irradiation time increased, the M values gradually increased and reached a plateau after several hours. After the M values reached a plateau, the magnetization values after irradiation, Ma, were measured at 2.0, 3.0, and 5.0 K in a field range of 0–50 kOe. The magnetization values of the sample before

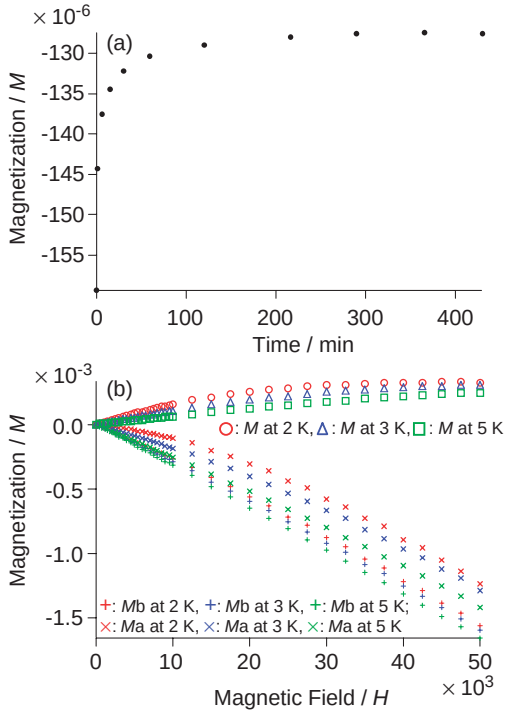


Fig. 4. (a) Plot of magnetization (M in emu) as a function of irradiation time observed in the photolysis of tris(diazo) compound **4**-3N_2 in 0.10 mM 2-methyltetrahydrofuran matrix measured at 5.0 K and 5 kOe. (b) Field dependence of the magnetization of the photoproduct from tris(diazo) compound **4**-3N_2 in 0.10 mM 2-methyltetrahydrofuran matrix measured at 2.0, 3.0, and 5.0 K. Ma and Mb refer to the magnetization value after and before irradiation, respectively, and $M = M\mathrm{a} - M\mathrm{b}$.

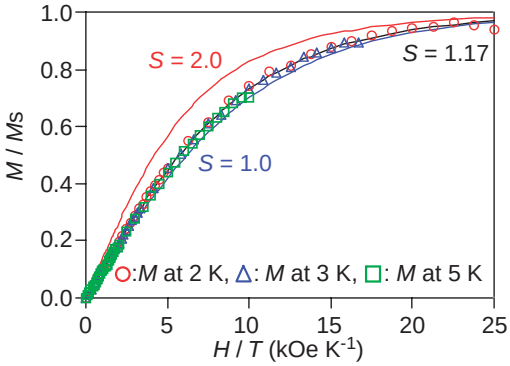


Fig. 5. Plots of M/Ms vs H/T of the photoproduct from tris(diazo) compound (**4**-3N_2) measured at 2.0 (○), 3.0 (△), and 5.0 (□) K. The solid lines represent theoretical curves with $S = 1.0$, 1.17, and 2.0.

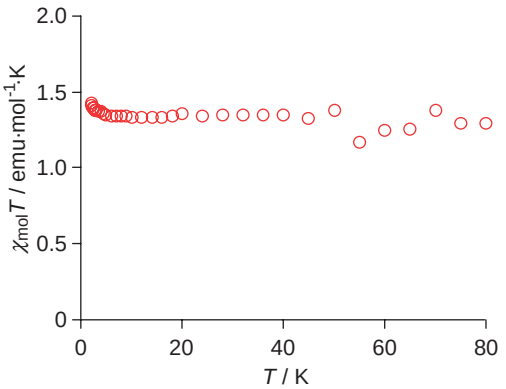


Fig. 6. Temperature dependence of the observed $\chi_{mol}T$ for the photoproduct from tris(diazo) compound (**4**-3N_2) obtained at a field of 0.1 T with a SQUID.

irradiation, Mb, were also measured under the same conditions. The magnetization (M) due to the species generated by photolysis was then obtained by subtracting the corresponding values obtained before and after irradiation (Fig. 4b). Thus, the effects of any paramagnetic impurities could be cancelled by this treatment. The plots of the magnetization normalized by the saturation magnetization (M/Ms) versus the temperature-normalized magnetic field (H/T) were analyzed in terms of the Brillouin function as follows:[1c,4,22]

$$M = M\mathrm{a} - M\mathrm{b} = FNgJ\mu_B B(\chi), \quad (1)$$

where F is the photolysis factor of the diazo compound, N is the number of the molecules, J is the quantum number for the total angular momentum, μ_B is the Bohr magneton, and g is the Landé g-factor. Since these carbenes are constituted of light elements, the orbital angular momentum should be negligible, and J can be replaced with the spin quantum number S. The M/Ms versus H/T plots are shown in Fig. 5, together with theoretical curves with $S = 1.0$, 1.17, and 2.0.[23]

The observed data for the photoproduct from the tris(diazo) compound (**4**-3N_2) followed the theoretical curve with $S = 1$. The observed data were fitted with Eq. 1 with $S = 1.17$ and $F = 1.05$. It is possible that, if the energy levels of triplet, quintet, and septet states are degenerate and, hence, the ferromagnetic interaction among the three carbene units is nearly zero, the plot of the magnetization normalized by the saturation magnetization can be fitted with $S = 1$. The fact that the observed value is slightly over one may suggest that the septet and/or quintet states lies slightly below the triplet ones (vide infra).

In order to examine magnetic interaction between the three carbene units, we obtained the magnetic susceptibility data for the photoproduct from **4**-3N_2 in the temperature range 2–80 K at a constant field of 100 mT. The temperature dependences of $\chi_{mol}T$ are given in Fig. 6. The $\chi_{mol}T$ value was approximately 1.4 emu K mol^{-1} at 80 K and remained almost constant in the temperature range down to 5 K when the temperature was lowered; the value increased very slightly at lower temperature. If there is no magnetic interaction between the three carbene units of tris(carbene) **4**, the χT value should become to be 3.0 emu K mol^{-1}. However, the experimental value is only 1.4 emu K mol^{-1}, which is smaller than one half of 3.0. Namely, the small χT value indicates that <50% of carbene units were generated under the irradiation conditions in the SQUID measurement. Although the value at 10 K was smaller than a theoretical value calculated for $S = 3$, the observed slight increase of the $\chi_{mol}T$ value under 5 K indicates that the three carbene units coupled to each other by a rather weak ferromagnetic interaction.

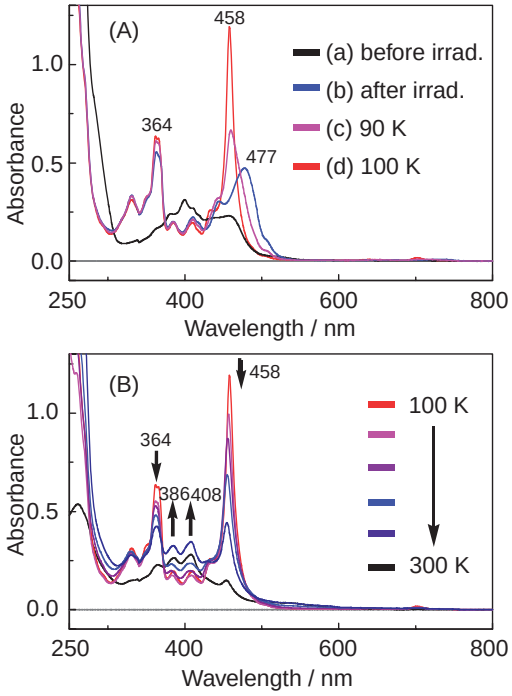


Fig. 7. UV–vis spectra obtained by irradiation of monodiazo compound **2**-N_2. (A) (a) Spectra of **2**-N_2 in 2-methyltetrahydrofuran at 77 K. (b) The same sample after irradiation ($\lambda > 350$ nm). (c–d) The same sample after thawing to 90 and 100 K. (B) UV–vis spectral change measured at 40 K increment upon warming the same sample from 100 to 300 K.

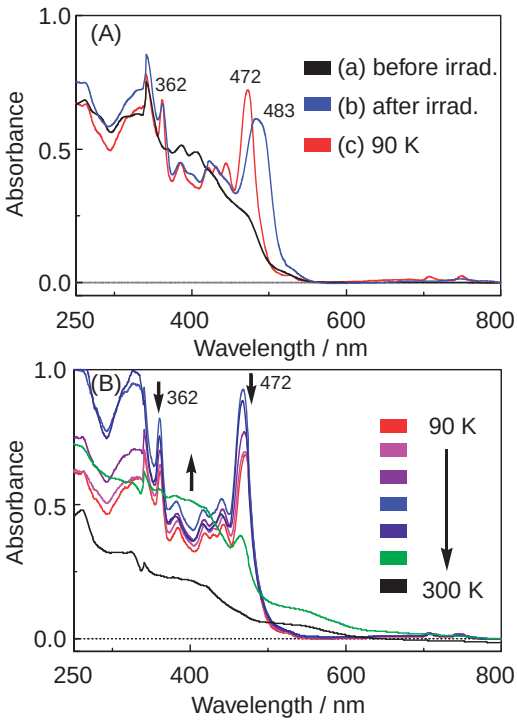


Fig. 8. UV–vis spectra obtained by irradiation of tris(diazo) compound **4**-3N_2. (A) (a) Spectra of **4**-3N_2 in 2-methyltetrahydrofuran at 77 K. (b) The same sample after irradiation ($\lambda > 350$ nm). (c) The same sample after thawing to 90 K. (B) UV–vis spectral change measured at 35 K increment upon thawing the same sample from 90 to 300 K.

UV–Vis Spectroscopic Study in a Matrix at Low Temperature. In order to examine the stability of those high-spin species in solution at room temperature, one should know the UV–vis spectroscopic feature of the species, since time-resolved UV–vis spectroscopy is most conveniently employed for such a study.[6,24]

Irradiation of a mono(diazo) compound (**2**-N_2) in a 2-MTHF matrix at 77 K resulted in rapid disappearance of the original absorption due to **2**-N_2 and concurrent growth of sharp and strong absorption bands at 364, 385, 414, 438, and 477 nm (Fig. 7). Since ESR signals ascribable to triplet carbene are observed under identical conditions, the absorption spectrum can be safely assigned to triplet carbene ^{3}**2**. When the matrix was gradually warmed, the bands became sharper, and at a longer wavelength, i.e., 477 nm, the bands shifted to 458 nm at around 90 K, and this new band increased up to 100 K. This change can be attributed to the geometrical change of the triplet carbene associated with a change in the viscosity of the matrixes upon annealing, as has been revealed in ESR experiments. Upon further thawing, the band started to disappear slowly at around 130 K but did not completely disappear even at 300 K.

These results are again to be compared with that observed for ^{3}**1**, which exhibited essentially identical absorption bands (362, 384, 412, 438, and 475 nm) but distinctly greater thermal stability.

Similar photolysis ($\lambda > 350$ nm) of a tris(diazo) compound (**4**-3N_2) in a 2-MTHF matrix at 77 K resulted in the rapid disappearance of the original absorption due to **4**-3N_2 and concurrent growth of sharp and strong absorption bands at 350, 362, 385, 430, and 483 nm (Fig. 8), which are very similar to those of monocarbene. Since ESR signals ascribable to tris(carbene) **4** are observed under identical conditions, the absorption spectrum can be safely assigned to **4**.

When the matrix was gradually warmed, the bands became sharper, and, at a longer wavelength, i.e., 483 nm, the bands shifted to 472 nm at around 90 K. This change was again attributed to the geometrical change of the triplet carbene associated with a decrease in the viscosity of the matrixes upon annealing. Upon further warming, the band started to increase with a slight shift to a shorter wavelength, and this change continued until the matrix temperature increased to 220 K. This observation suggests that geometrical changes of tris(carbene) **4** are not completed until 220 K. This can be compared with the fact that a similar change in the UV–vis spectra of monocarbene **2** is completed at around 100 K. The difference is interpreted to indicate that the geometrical relaxation of tris(carbene) requires much more enhanced fluidness of the matrix at higher temperature than that of monocarbene **2**. This difference can also be interpreted to indicate that the molecular motion associated with geometrical relaxation of three units of a congested dianthrylcarbene is more complex than that with a single unit.

The absorption bands began to disappear at 260 K and completely vanished at around 300 K. Anomalous thermal stability was again noted.

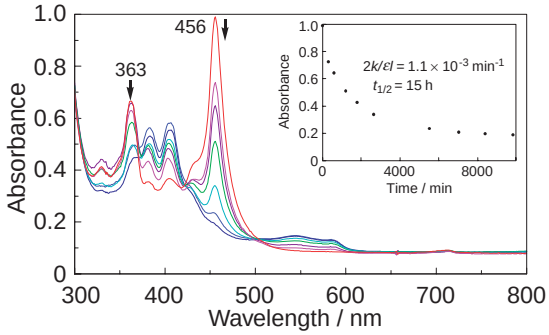


Fig. 9. Absorption of transient products formed during irradiation of monodiazo compound **2**-N_2 in degassed benzene at room temperature recorded 0, 5, 10, 20, 44, 92, and 140 h after excitation. Inset shows the time course of the absorption at 456 nm.

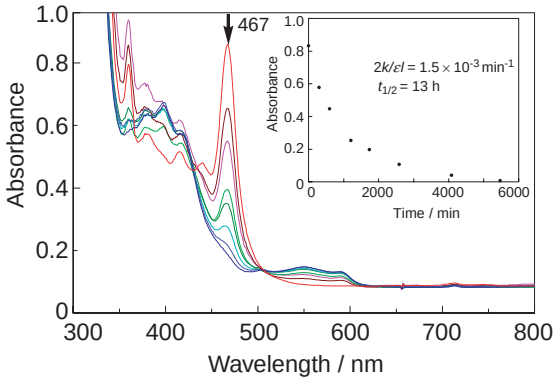


Fig. 10. Absorption of transient products formed during irradiation of tris(diazo) compound **4**-3N_2 in degassed benzene at room temperature recorded 0, 5, 10, 20, 29, 68, 91, and 98 h after excitation. Inset shows the time course of the absorption at 467 nm.

Time-Resolved UV–Vis Spectroscopic Study in Solution at Room Temperature. In order to determine the stability of the present carbenes more accurately, we estimated the lifetime in a degassed benzene at room temperature, in which we measured the lifetime of a series of sterically congested diarylcarbenes.[6] The lifetime of the present carbenes was too long to monitor with a laser flash photolysis technique, which is routinely used in such studies; therefore, it was more convenient to use a conventional UV–vis spectroscopic method in this case.

Brief irradiation of the mono(diazo) compound (**2**-N_2) in degassed benzene at 20 °C with a 70–90 mJ, 308 nm pulse from a XeCl excimer laser produced transient absorption bands showing strong maxima at 363 and 456 nm, which appeared coincidently with the pulse (Fig. 9). These transient absorption bands are essentially the same as those observed in the photolysis of **2**-N_2 in 2-MTHF matrix at 77 K, followed by warming to 100 K. Thus, we assigned the transient product to ^{3}**2** in its geometrically relaxed state. The absorption bands decayed very slowly, and the transient bands did not disappear completely even after the material was kept for several hours under these conditions. The decay was found to be of the second order ($2k/\varepsilon l = 1.1 \times 10^{-3}$ min^{-1}). In accordance with the kinetic observation, the MS analysis of the spent solution indicated the presence of a peak at 1531.72 m/z, corresponding to the dimer of the carbene as a major peak (Fig. S4).[25] The approximate half-life ($t_{1/2}$) of ^{3}**2** was estimated to be 15 hours. This is shorter-lived than ^{3}**1**, whose half-life is estimated to be 14.5 days,[12b] but still fairly stable for a triplet carbene.

Similar irradiation of the tris(diazo) compound (**4**-3N_2) also produced transient absorption bands showing strong maxima at 362 and 467 nm (Fig. 10). Again, the transient absorption bands were essentially the same as those observed for tris(carbene) **4** in its relaxed state. The fact that the molecular extinction coefficient ($\varepsilon = 4.83 \times 10^4$ mol^{-1} cm^{-1} dm^3) of this species was roughly three times as large as that observed for ^{3}**1** ($\varepsilon = 1.83 \times 10^4$ mol^{-1} cm^{-1} dm^3) indicates that the transient bands are due to tris(carbene) **4** rather than to a monocarbene generated by incomplete decomposition of **4**-3N_2. This is further supported by the finding that analysis of the spent solution by IR spectroscopy did not indicate the presence of any characteristic band due to the diazo group. Again, the transient bands decayed very slowly in a second-order fashion ($2k/\varepsilon l = 1.5 \times 10^{-3}$ min^{-1}). The approximate half-life ($t_{1/2}$) of **4** was estimated to be 13 hours, indicating that the stability of a unit monocarbene is maintained in tris(carbene).

Spin State of Tris(carbene) 4. Ovchinnikov has derived a method for predicting the ground-state multiplicity of alternant hydrocarbons based on valence bond theory by counting starred and unstarred carbons.[26] His conclusion is expressed in terms of Eq. 2,

$$S = (n^* - n)/2, \tag{2}$$

where n^* and n are the number of starred and unstarred carbons, respectively. When triplet carbenes, which have spin quantum number $S = 1$, are used as spin sources, Eq. 2 can be rewritten as follows:

$$S = n^* - n. \tag{3}$$

If this method is applied to predict the ground-state multiplicity of tris(carbene) **4**, in Scheme 3, the numbers of starred and unstarred carbon are 24 and 21, respectively, and, hence, $S = 3$ is predicted.

However, the ground-state multiplicity of the tris(carbene) should be examined in terms of the connectivity.[27] The nonbonding molecular orbitals (NBMOs) of **4** are studied by means of the simple Hückel molecular orbital method, in which the atoms having nonzero NBMO coefficients are starred. To a first approximation, the spin densities are assumed to be generated on the atoms with such nonzero coefficients. However, the ethynyl groups in **4**, which connect dianthrylcarbene to the central phenyl ring, are introduced on the anthryl group at sites of very small spin density (orbital nodes). Therefore, in **4**, the coefficients in NBMOs in the atoms in the bridging group are nearly zero. In other words, the NBMOs are mostly localized in three dianthrylcarbene moieties. The magnitude of these spin interactions is thus expected to be very small.

Connectivity across nodal (inactive) sites is typical for many systems that are disjoint in the Borden/Davidson sense.[28,29] Many of these systems have singlet ground states with low-lying high spin states.[30,31] Experimentally, in these systems,

signals due to a higher-spin state are detected by ESR, but the signal intensities deviate from the Curie law. However, in the present case, the intensities of signals due to both triplet and higher-spin state(s) decreased linearly with the reciprocal of the temperature, in good agreement with the Curie law[18] at least up to 10 K. If one assumes that all signals originate from tris(carbene), it could be interpreted that all states, including singlet states, are degenerate or lie close to each other. In other words, the exchanging coupling constant (J) is extremely small or nearly zero.[32] This may be partly because of small spin densities in the dianthrylcarbene as a result of extensive delocalization.[12,33]

The SQUID measurements also support the small interaction. Namely, the slight increase of the $\chi_{mol}T$ value under 5 K indicates that the three carbene units in the tris(carbene) coupled by an extremely small ferromagnetic interaction. Moreover, the fact that the observed spin quantum number is slightly over unity may suggest that all the states of the tris(carbene) are almost degenerate, but that the septet and/or quintet states lies slightly below the triplet ones.

Analogous spin systems are not unprecedented. For instance, 1,1,2,2-tetramethyl-1,2-di(3-nitrenophenyl)disilane showed ESR signals of both triplet and quintet states, and the signal intensities followed Curie's law in the range of 10–64 K. This is interpreted to indicate that the spin states are nearly degenerate with $0 > \Delta E_{S\text{-}Q} > -3.4$ cal/mol.[30c] However, in this system, ZFS parameters for the triplet state of bis(nitrene) are not identical with those of triplet mononitrene.

It is to be noted here that, in the variable-temperature study of ESR signals (Fig. 2), the signals at around 310–325 mT started to decrease rather sharply at around 280 K and disappeared almost completely at 300 K, while the signals due to triplet species remained mostly unchanged even at 280 K. This suggests that triplet signals and signals at around 310–325 mT are probably not arising from the same species. In accord with this suggestion, we found that the intensities of the signals of the two states depend on the wavelength of the irradiating light. Thus, irradiation of **4**-$3N_2$ with a longer-wavelength light ($\lambda > 450$ nm) gave mainly signals due to the triplet species, while irradiation with a shorter wavelength light ($\lambda >$ 350 nm) gave the signals of both states.

If tris(diazo) compound (**4**-N_2) is decomposed in stepwise manner, bis(diazo)monocarbene will be initially formed. Since monocarbene **1** formed by photolysis of mono(diazo) compound **1**-N_2 exhibits rather strong absorption bands around 450 nm, a longer wavelength than that of the precursor **1**-N_2, the monocarbene is also expected to have strong absorption bands in visible region where the diazo group has no remarkable absorption band. Thus irradiation of tris(diazo) compound (**4**-N_2) with the wavelength longer than 450 nm is expected to produce the monocarbene to a significant extent. On the other hand, monocarbene **1** has no strong absorption band in the region of 370–420 nm. Thus, irradiation of tris(diazo) compound (**4**-N_2) with the wavelength longer than 350 nm is expected to decompose the monocarbene to generate bis- and tris-carbenes. Therefore, it is reasonable that a mixed spectrum of a monocarbene and high-spin species (a bis(carbene) and a tris(carbene)) is observed upon >350 nm irradiation.

Judging from these observations, we think it is likely that the triplet signals and the other ones are originating from two different species. From ZFS parameters (E/D) for triplet signals, it is mostly likely that the signals are due to triplet monocarbene, not due to tris(carbene).[33]

The computer simulation did not discriminate between the signals for triplet ^{3}**4**, quintet ^{5}**4**, and septet states ^{7}**4** (Fig. S3). It may be, then, that the signals around 310–325 mT in Fig. 2 consist of triplet, quintet, and septet states which are all nearly degenerate.

Conclusion

The present investigation demonstrates that the preparation of usable high-spin organic materials employing a stable triplet carbene unit as a spin source is an achievable objective.

In the present system, the main reason why the high-spin states are not exclusively generated and the S value is remarkably smaller than the theoretical one is that the connectivity was wrong; however, it would be possible to generate septet tris(carbene) by connecting the anthryl carbene unit at either the 2 or the 4 position. All attempts so far to prepare the desired tris(diazo) compounds by using the Sonogashira coupling reaction, however, have been unsuccessful. This is partly because of steric reasons, as molecular models suggest that connecting three dianthryl units from these positions causes more steric hindrance in the resulting tris(diazo) compounds than **4**-$3N_2$. However, there are other ways to connect diazo units to a linker. One way to realize this is to introduce a bridging ligand, which makes a polymeric chain structure by the ligation with metal ions. For instance, diazo(di-4-pyridyl)methane formed a 1:1 complex with bis(hexafluoroacetylacetonato)copper(II) [$Cu(hfac)_2$]. Upon photolysis, this complex generated a ferromagnetic chain with the apparent spin quantum number of 33 as a result of ferromagnetic interaction between the 3d spin of Cu(II) and 2p spins of di(4-pyridyl)carbene.[3,34] This suggests that once pyridyl groups are introduced into a sterically congested diazomethane, a precursor for a persistent triplet carbene, it may be possible to prepare a complex with metal ions that can generate a persistent high-spin polycarbene.

The finding that a precursor diazo unit can basically be handled as a building block to construct poly-diazo compounds makes such a project very realistic. Thus, the building block could very easily be introduced on properly designed π-topological linkers ad libitum. In other words, a poly-diazo compound designed to generate a desired high-spin polycarbene can be prepared with great ease. A starburst nona(diazo) compound, for instance, was prepared by trimerization of aryl ethynyl ketone, followed by oxidation, hydrazonation of the resulting nona-ketone, and poly-oxidation.[4] The method is elegant, but it is not applicable to other more complicated systems, including sterically congested derivatives.

The study also reveals that persistent triplet carbenes, even though they lose most of their typical reactivity as a triplet carbene, still retain electronic properties and act as a spin source when aligned properly in the π-electron frameworks to generate a high-spin molecule, just as a prototypical triplet carbene does.

Most importantly, polycarbenes consisting of a persistent triplet carbene are also very persistent, surviving up to 300 K and for up to a day in solution at room temperature. Moreover,

undesirable bimolecular side reactions, which generate chemical defects among the topologically controlled high-spin ($S = 1$) centers for extended spin alignment, are rigorously avoided.

Although high-spin organic materials with the lifetime of a day are still ephemeral for practical use, in the light of the fact that a more persistent triplet carbene surviving for days under ambient conditions is close to being realized, it will not be long before a stable high-spin polycarbene is available.

Experimental

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JM-AL300FT/NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. IR spectra were measured on a JASCO FT/IR-410 spectrometer, and UV–vis spectra were recorded on a JASCO CT-560 spectrophotometer. ESR spectra were measured on a JEOL JES-TE200D ESR spectrometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer and an AB Voyager-DE PRE MALDI-TOF mass spectrometer. Gel permeation chromatography (GPC) was carried out on a JASCO model HLC-01 instrument. The GPC column was a Shodex H-2001. Thin-layer chromatography was carried out on a Merck Kieselgel 60 PF254. Column chromatography was performed on silica-gel (Kanto Chemical) for column chromatography or ICN alumina (ICN Biomedicals) for dry column chromatography.

Preparation of [3-Bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]diazomethane (2-N_2). (a) Preparation of 9-(4-*t*-Butyl-2,6-dimethylphenyl)anthracene: To a solution of 4-*t*-butyl-2,6-dimethylbromobenzene[35] (5.0 g, 20.7 mmol) in anhydrous diethyl ether (40 mL) was added 1.4 M *t*-butyllithium in pentane (30.4 mL, 45.6 mmol) at −78 °C under nitrogen atmosphere. The mixture was stirred for 30 min at −78 °C and allowed to warm up to room temperature. To this mixture, a solution of the anthrone[36] (4.0 g, 20.7 mmol) in anhydrous toluene (100 mL) was added, and the mixture was refluxed overnight. To the mixture allowed to cool to room temperature, a saturated ammonium chloride aqueous solution was added carefully. The reaction mixture was extracted with diethyl ether, and the organic layer was washed with water, and dried over anhydrous sodium sulfate. A brown solid obtained after concentration of the solution was chromatographed on a silica-gel column eluted with hexane to afford a crude product, which was purified by a short-path distillation (85 °C/1.0 mmHg). 9-(4-*t*-Butyl-2,6-dimethylphenyl)anthracene was obtained as a pale-yellow solid in 53% yield (3.7 g): mp 167 °C. ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 9H), 1.64 (s, 6H), 7.15 (s, 2H), 7.20 (ddd, $J = 8.45$, 6.43, 1.10 Hz, 2H), 7.32 (ddd, $J = 8.45$, 6.43, 1.29 Hz, 2H), 7.37 (d, $J = 8.82$ Hz, 2H), 7.93 (d, $J = 8.45$ Hz, 2H), 8.35 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 20.4, 31.6, 34.5, 124.4, 125.1, 125.5, 126.0, 126.1, 128.6, 129.8, 131.6, 134.4, 136.0, 137.0, 150.3. IR (KBr, cm^{-1}) 3051m, 3024w, 2961s, 2949s, 2921w, 2899w, 2862m, 1622vw, 1607w, 1575w, 1517w, 1478w, 1440m, 1408vw, 1374w, 1362m, 1302w, 1231w, 1189m, 1161vw, 1013m, 953w, 946m, 877s, 839s, 791m, 733vs, 652m, 606m, 561w, 513w. MS m/z (relative intensity) 338 (M^+, 100), 323 (41.2); HRMS calcd for $C_{26}H_{26}$ 338.2035, found m/z 338.2034.

(b) Preparation of 9-Bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)anthracene: A solution of the phenylanthracene (3.5 g, 10.34 mmol) in carbon tetrachloride (40 mL) was cooled to 0 °C. To this mixture, a carbon tetrachloride solution (3 mL) of bromine (0.56 mL, 11.37 mmol) was added dropwise at 0 °C, and the mixture was stirred at room temperature overnight. To this mixture, an aqueous solution of 10% sodium hydroxide was added carefully. The reaction mixture was extracted with carbon tetrachloride, and the organic layer was washed with water, and dried over anhydrous sodium sulfate. After removal of the solvent, the resulting crude product was washed with hexane to afford 9-bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)anthracene (3.7 g, 86%) as a yellow crystal: mp 180 °C. ^{1}H NMR ($CDCl_3$): δ 1.44 (s, 9H), 1.72 (s, 6H), 7.24 (s, 2H), 7.35 (ddd, $J = 8.82$, 6.43, 1.29 Hz, 2H), 7.48 (dd, $J = 8.82$, 1.29 Hz, 2H), 7.57 (ddd, $J = 8.82$, 6.43, 1.29 Hz, 2H), 8.60 (dd, $J = 8.82$, 1.10 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.4, 31.5, 34.5, 122.1, 124.5, 125.8, 126.5, 127.0, 128.0, 130.5, 130.6, 134.0, 136.8, 150.7. IR (KBr, cm^{-1}) 3065w, 2960s, 2951m, 2862m, 1605w, 1559w, 1540vw, 1507vw, 1437s, 1374vw, 1362m, 1341m, 1300w, 1256m, 1229vw, 1190w, 1148w, 1026m, 945s, 915m, 877w, 866w, 845w, 784w, 756vs, 652s, 605w, 577w. MS m/z (relative intensity) 418 ($M + 2$, 31.3), 416 (M^+, 31.7), 338 (100), 323 (38.5); HRMS calcd for $C_{26}H_{25}Br$ 416.1139, found m/z 416.1125.

(c) Preparation of 10-(4-*t*-Butyl-2,6-dimethylphenyl)anthracene-9-carbaldehyde: To a solution of the bromide (2.0 g, 4.79 mmol) in anhydrous diethyl ether (10 mL) was added 2.6 M butyllithium in hexane (2.2 mL, 5.75 mmol) at 0 °C under nitrogen atmosphere. Then the mixture was stirred for 2 h at 0 °C. Absolute DMF (1.12 mL, 14.37 mmol) was added to the lithiated mixture at 0 °C, and the mixture was refluxed overnight. The mixture was allowed to cool to room temperature, and a saturated ammonium chloride aqueous solution was added carefully. Insoluble material was filtered and washed with water to give a crude aldehyde (1.4 g). The filtrate was extracted with diethyl ether, and the organic layer was washed with water, dried over anhydrous sodium sulfate and evaporated to leave a crude product (0.7 g). The combined crude product was chromatographed on a silica-gel column eluted with hexane/dichloromethane (1:1). 10-(4-*t*-Butyl-2,6-dimethylphenyl)anthracene-9-carbaldehyde was obtained as a yellow solid in 57% yield (1.0 g): mp 218 °C. ^{1}H NMR ($CDCl_3$): δ 1.44 (s, 9H), 1.72 (s, 6H), 7.24 (s, 2H), 7.38–7.43 (m, 2H), 7.56 (d, $J = 8.82$ Hz, 2H), 7.64–7.69 (m, 2H), 9.04 (d, $J = 9.00$ Hz, 2H), 11.60 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 20.3, 31.5, 34.5, 123.7, 124.59, 124.60, 125.9, 127.1, 128.8, 129.4, 131.9, 133.9, 136.3, 145.4, 151.0, 193.4. IR (KBr, cm^{-1}) 3066w, 3044w, 2960s, 2915w, 2864m, 2765w, 1680vs ($\nu_{C=O}$), 1607vw, 1556m, 1483w, 1438m, 1406vw, 1362w, 1270m, 1230vw, 1190m, 1152w, 1048m, 1029vw, 945m, 900w, 876w, 799w, 758m, 753m, 734w, 662m, 642vw, 602w, 569vw. MS m/z (relative intensity) 366 (M^+, 100), 351 (36.9); HRMS calcd for $C_{27}H_{26}O$ 366.1984, found m/z 366.1986.

(d) Preparation of 2-Bromo-9-(4-*t*-butyl-2,6-dimethylphenyl)anthracene: To a solution of 4-*t*-butyl-2,6-dimethylbromobenzene (2.5 g, 10.3 mmol) in anhydrous diethyl ether (10 mL) was added 1.4 M *t*-butyllithium in pentane (15.0 mL, 22.6 mmol) at −78 °C under nitrogen atmosphere. The mixture was stirred for 30 min at −78 °C and allowed to warm up to room temperature. To this mixture, a solution of 2-bromoanthrone[37] (2.8 g, 10.3 mmol) in anhydrous toluene (100 mL) was added, and the mixture was refluxed overnight. The mixture was allowed to cool to room temperature, and a saturated ammonium chloride aqueous solution was added carefully. The reaction mixture was extracted with diethyl ether, and the organic layer was washed with water and dried over anhydrous sodium sulfate. A brown solid obtained after concentration of the solution was chromatographed on a silica-gel column eluted with hexane to afford a crude product, which was

purified by a short-path distillation (85 °C/1.0 mmHg). 2-Bromo-9-(4-*t*-butyl-2,6-dimethylphenyl)anthracene was obtained as a pale yellow solid in 38% yield (1.6 g): mp 188 °C. ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 9H), 1.72 (s, 6H), 7.24 (s, 2H), 7.30–7.51 (m, 4H), 7.63 (s, 1H), 7.92 (d, $J = 9.00$ Hz, 1H), 8.03 (d, $J = 8.45$ Hz, 1H), 8.43 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 20.4, 31.5, 34.5, 120.0, 124.6, 125.6, 126.1, 126.2, 126.3, 127.7, 128.6, 128.7, 129.8, 130.3, 130.4, 130.6, 131.7, 133.6, 135.5, 136.8, 150.6.

(e) Preparation of 2,10-Dibromo-9-(4-*t*-butyl-2,6-dimethylphenyl)anthracene: A solution of 2-bromo-9-(4-*t*-butyl-2,6-dimethylphenyl)anthracene (1.0 g, 2.40 mmol) in carbon tetrachloride (15 mL) was cooled to 0 °C. To this mixture, a carbon tetrachloride solution (2 mL) of bromine (0.13 mL, 2.64 mmol) was added dropwise at 0 °C, and the mixture was stirred at room temperature overnight. To this mixture, an aqueous solution of 10% sodium hydroxide was added carefully. The reaction mixture was extracted with carbon tetrachloride, and the organic layer was washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the resulting crude product was washed with hexane to afford 2,10-dibromo-9-(4-*t*-butyl-2,6-dimethylphenyl)anthracene (1.0 g, 87%) as a yellow solid: mp 210 °C. ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 9H), 1.72 (s, 6H), 7.25 (s, 2H), 7.35–7.45 (m, 2H), 7.58–7.63 (m, 2H), 7.64 (s, 1H), 8.49 (d, $J = 9.00$ Hz, 1H), 8.57 (d, $J = 8.46$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 20.4, 31.5, 34.5, 120.6, 122.5, 124.8, 126.51, 126.55, 127.5, 127.9, 128.1, 128.8, 130.1, 130.5, 130.7, 131.2, 131.3, 133.2, 136.2, 136.7, 151.0. IR (KBr, cm^{-1}) 3069w, 2958vs, 2916w, 2899w, 2860m, 1604m, 1546w, 1512vw, 1438s, 1374vw, 1361m, 1351w, 1323s, 1299w, 1255vw, 1228vw, 1186m, 1161vw, 1065m, 1026vw, 947vs, 915s, 874m, 849vw, 803s, 777s, 754vs, 719m, 664m, 652m, 579m, 511w. MS m/z (relative intensity) 498 ($M + 4$, 50.3), 496 ($M + 2$, 100), 494 (M^+, 52.9); HRMS calcd for $C_{26}H_{24}Br_2$ 494.0244, found m/z 494.0242.

(f) Preparation of [3-Bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]-methanol: To a solution of 2,10-dibromo-9-(4-*t*-butyl-2,6-dimethylphenyl)anthracene (600 mg, 1.21 mmol) in anhydrous diethyl ether (8 mL) was added 2.6 M butyllithium in hexane (0.48 mL, 1.21 mmol) at 0 °C under nitrogen atmosphere and the mixture was stirred for 2 h at 0 °C. A solution of 10-(4-*t*-butyl-2,6-dimethylphenyl)anthracene-9-carbaldehyde (443 mg, 1.21 mmol) in anhydrous tetrahydrofuran (8 mL) was added to the lithiated mixture at 0 °C, and the mixture was heated overnight at 40 °C. The mixture was allowed to cool to room temperature, and a saturated ammonium chloride solution was added carefully. The reaction mixture was extracted with diethyl ether, and the organic layer was washed with water, dried over anhydrous sodium sulfate and evaporated. The crude product was recrystallized from dichloromethane–hexane to give [3-bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]methanol (535 mg, 56%) as a yellow solid: mp 247–250 °C. ^{1}H NMR ($CDCl_3$): δ 1.448 (s, 9H), 1.452 (s, 9H), 1.76 (s, 6H), 1.77 (s, 6H), 2.97 (d, $J = 3.12$ Hz, 1H), 7.19–7.28 (m, 7H), 7.227 (s, 2H), 7.233 (s, 2H), 7.45–7.55 (m, 3H), 7.65 (d, $J = 2.02$ Hz, 1H), 8.52–8.57 (m, 4H), 8.67 (d, $J = 2.94$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 20.3, 31.5, 31.6, 34.49, 34.51, 73.0, 119.6, 124.5, 124.7, 125.0, 125.3, 125.6, 126.0, 126.2, 127.1, 127.2, 127.8, 128.4, 128.9, 130.0, 130.2, 130.6, 133.8, 134.1, 134.7, 136.7, 136.8, 137.4, 138.5, 143.9, 144.1, 150.5, 150.7. IR (KBr, cm^{-1}) 3519m (ν_{O-H}), 3062w, 2960vs, 2921m, 2865m, 1604m, 1559w, 1540w, 1522w, 1507w, 1477m, 1457w, 1442s, 1407vw, 1393vw, 1362s, 1288vw, 1228m, 1191w, 1071m, 1042m, 977w, 944s, 902m, 869m, 815m, 802m, 780s, 768s, 728vw, 706w, 676w, 664m, 626w, 610w, 588w, 569w, 556w, 526w, 511w. MS m/z (relative intensity) 784 ($M + 2$, 46.3), 783 (36.5), 782 (M^+, 59.1), 445 (50.6), 443 (49.7), 366 (64.8), 365 (100); HRMS calcd for $C_{53}H_{51}BrO$ 782.3123, found m/z 782.3196.

(g) Preparation of [3-Bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]chloromethane: Into a solution of the methanol (600 mg, 0.77 mmol) in anhydrous benzene (20 mL) cooled to 0 °C, a hydrogen chloride gas generated by adding hydrochloric acid (3 mL) to sulfuric acid (4.5 mL) was bubbled for 15 min and the mixture was stirred for 1 h at 0 °C. Removal of the solvent afforded [3-bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]chloromethane (615 mg, quantitatively) as a brown viscous liquid as a crude product. This was used without further purification since the chloride was found to be rather unstable. ^{1}H NMR ($CDCl_3$): δ 1.45 (brs, 18H), 1.77 (brs, 12H), 7.16–7.36 (m, 11H), 7.45–7.54 (m, 1H), 7.51–7.55 (m, 2H), 7.65 (d, $J = 1.42$ Hz, 1H), 8.54–8.57 (m, 4H), 8.67 (s, 1H).

(h) Preparation of Ethyl [3-Bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]methylcarbamate: A solution of the chloromethane (615 mg, 0.77 mmol) in anhydrous 1,4-dioxane (30 mL) was added to a molten mixture of silver tetrafluoroborate (204 mg, 1.12 mmol) and urethane (1.30 g, 15.4 mmol) at 60 °C. After addition was completed, the mixture was refluxed overnight. After cooling, silver chloride was removed from the reaction mixture by filtration and washed with dichloromethane. The filtrate was washed with water and the organic layer was dried over anhydrous sodium sulfate and evaporated. The crude product was chromatographed on a silica-gel column eluted with hexane/dichloromethane (1:1). Ethyl [3-bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]methylcarbamate was obtained as an ocherous solid in 67% yield (440 mg): mp 187–190 °C. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, $J = 7.04$ Hz, 3H), 1.44 (brs, 18H), 1.73 (brs, 12H), 4.20 (q, $J = 6.92$ Hz, 2H), 5.94 (d, $J = 7.72$ Hz, 1H), 7.24 (s, 4H), 7.25–7.38 (m, 4H), 7.43–7.52 (m, 5H), 7.64 (d, $J = 1.84$ Hz, 1H), 8.42–8.48 (m, 5H), 8.69 (d, $J = 6.80$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.7, 20.3, 31.5, 34.5, 54.6, 61.4, 119.5, 124.2, 124.4, 124.7, 124.9, 125.5, 126.2, 126.6, 127.3, 127.4, 128.3, 128.7, 129.1, 130.0, 130.2, 130.6, 131.0, 133.0, 133.95, 134.01, 134.7, 136.8, 137.2, 138.2, 150.5, 150.7, 155.3. IR (KBr, cm^{-1}) 3455w (ν_{N-H}), 3063w, 2963vs, 2867m, 1725vs ($\nu_{C=C}$), 1604m, 1570vw, 1495s, 1480s, 1443s, 1407w, 1393vw, 1376w, 1362m, 1324w, 1303w, 1276vw, 1228s, 1172vw, 1094vw, 1043m, 998vw, 944s, 900w, 868m, 816w, 803w, 763s, 754s, 703vw, 659m, 646vw, 606vw. MS m/z (relative intensity) 855 ($M + 3$, 52), 854 ($M + 2$, 100), 853 ($M + 1$, 70), 852 (M^+, 92), 767 (67), 765 (60); HRMS calcd for $C_{56}H_{55}BrNO_2$ 852.3411, found m/z 852.3357

(i) Preparation of [3-Bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]diazomethane (2-N_2): Some dinitrogen tetraoxide (1.7 g, 18.91 mmol) was bubbled into anhydrous carbon tetrachloride (10 mL) which had been cooled to −20 °C. After sodium acetate (3.1 g, 37.82 mmol) was added to this mixture, a solution of the carbamate (135 mg, 0.16 mmol) in anhydrous carbon tetrachloride (5 mL) was added at −20 °C and the mixture was stirred for 2 h at 0 °C. The reaction mixture was then poured into crushed ice and extracted with carbon tetrachloride. The organic layer was washed with aqueous sodium hydrogencarbonate and water and dried over anhydrous sodium sulfate. A brown solid obtained after

concentration of the solution was mixed with anhydrous tetrahydrofuran (5 mL) under nitrogen atmosphere and the mixture was cooled to −20 °C. Potassium *t*-butoxide (38 mg, 0.32 mmol) was added and the mixture was stirred overnight at room temperature. The reaction mixture was extracted with diethyl ether, and the organic layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by GPC (7 cycles, chloroform as eluent), and then by TLC with hexane/dichloromethane (1:2) as eluent to give [3-bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]diazomethane (**2**-N_2) (51 mg, 40%) as an orange viscous liquid. ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 9H), 1.46 (s, 9H), 1.78 (s, 12H), 7.27 (s, 4H), 7.30–7.43 (m, 7H), 7.53 (d, J = 8.64 Hz, 1H), 7.57 (d, J = 9.37 Hz, 2H), 7.69 (d, J = 2.02 Hz, 1H), 8.18 (d, J = 9.55 Hz, 1H), 8.27 (d, J = 7.90 Hz, 2H), 8.34 (d, J = 8.64 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 20.37, 20.40, 31.5, 31.6, 34.5, 56.4, 120.2, 124.5, 124.8, 125.3, 125.5, 126.2, 126.6, 127.3, 127.4, 128.3, 128.7, 129.1, 130.0, 130.20, 130.25, 130.3, 131.0, 131.3, 133.7, 134.4, 136.8, 136.9, 137.2, 138.3, 150.6, 150.8. IR (NaCl, cm^{-1}) 3062w, 2963s, 2865w, 2039vs ($\nu_{C=N2}$), 1604w, 1440m, 1409w, 1388w, 1362w, 1303w, 1228w, 1187w, 1028w, 967vw, 946s, 907s, 868w, 819w, 809vw, 784vw, 765m, 733s.

Preparation of Tris(diazo) Compound (4-3N_2). (a) Preparation of [10-(4-*t*-Butyl-2,6-dimethylphenyl)-9-anthryl][3-trimethylsilylethynyl-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]diazomethane (3-N_2(TMS)): The diazo compound (**2**-N_2) (30 mg, 0.038 mmol) and catalytic amounts of [$PdCl_2(Ph_3P)_2$] and copper(I) iodide were mixed with anhydrous tetrahydrofuran (0.7 mL) under nitrogen atmosphere. To this mixture, anhydrous triethylamine (0.3 mL) and trimethylsilylacetylene (0.05 mL, 0.30 mmol) were added successively, and the mixture was stirred overnight at 40 °C. After cooling, catalysts were removed from the reaction mixture by filtration through a short alumina column (hexane). After evaporation of the solvent, the residue was purified by GPC (overnight, chloroform as eluent) to afford [10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][3-trimethylsilylethynyl-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]diazomethane **3**-N_2(TMS) (12.7 mg, 41%) as an orange viscous liquid. ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 9H), 1.45 (s, 9H), 1.46 (s, 9H), 1.78 (brs, 12H), 7.27 (s, 2H), 7.28 (s, 2H), 7.31–7.37 (m, 7H), 7.47–7.57 (m, 3H), 7.69 (d, J = 0.92 Hz, 1H), 8.24 (d, J = 9.74 Hz, 1H), 8.27 (d, J = 9.16 Hz, 2H), 8.31 (d, J = 8.64 Hz, 1H). IR (NaCl, cm^{-1}) 3063w, 2963s, 2866w, 2151w ($\nu_{C\equiv C}$), 2038vs ($\nu_{C=N2}$), 1636w, 1477w, 1438w, 1362w, 1250m, 1228w, 1027w, 986w, 944w, 859s, 843s, 760s, 668w.

(b) Preparation of [3-Ethynyl-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]diazomethane (3-N_2): To a solution of the diazomethane **3**-N_2(TMS) (12.7 mg, 0.015 mmol) in *t*-butyl alcohol (3 mL) was added 10% aqueous solution (1 mL) of sodium hydroxide, and the mixture was stirred overnight at room temperature. The reaction mixture was extracted with diethyl ether; then the organic layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by GPC (overnight, chloroform as eluent) to afford [3-ethynyl-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]diazomethane (**3**-N_2). (11 mg, quantitatively) as an orange viscous liquid. ^{1}H NMR ($CDCl_3$): δ 1.45 (brs, 18H), 1.78 (brs, 12H), 3.08 (s, 1H), 7.27 (brs, 4H), 7.30–7.39 (m, 7H), 7.52–7.58 (m, 3H), 7.76 (s, 1H), 8.24 (d, J = 9.74 Hz, 1H), 8.27 (d, J = 9.16 Hz, 2H), 8.31 (d, J = 8.64 Hz, 1H). IR (NaCl, cm^{-1}) 3302m ($\nu_{\equiv C-H}$), 3062w, 2965vs, 2926m, 2866m, 2248w ($\nu_{C\equiv C}$), 2039vs ($\nu_{C=N2}$), 1740w, 1636vw, 1606vw, 1439m, 1362m, 1281w, 1229m, 1191vw, 1138w, 1100w, 1029m, 944m, 908s, 869m, 824m, 765m, 735s, 651w.

(c) Preparation of Tris(diazo) Compound (4-3N_2): The diazomethane **3**-N_2 (35 mg, 0.047 mmol), 1,3,5-triiodobenzene (6.5 mg, 0.016 mmol) and catalytic amounts of [$PdCl_2(Ph_3P)_2$] and copper(I) iodide were mixed with anhydrous tetrahydrofuran (1 mL) under nitrogen atmosphere. To this mixture, anhydrous triethylamine (0.5 mL) was added and this combination was stirred overnight at room temperature. Removal of the catalyst by filtration through a short alumina column, followed by removal of the solvent, gave crude material which was purified by GPC (8 cycles, chloroform as eluent) and TLC (CH_2Cl_2:hexane = 1:1) to give tris(diazo) compound (**4**-3N_2) (9 mg, 25%) as an orange viscous liquid. ^{1}H NMR ($CDCl_3$): δ 1.46 (brs, 54H), 1.79 (brs, 36H), 7.28 (brs, 12H), 7.30–7.41 (m, 21H), 7.51 (d, J = 8.82 Hz, 3H), 7.54 (s, 3H), 7.58 (d, J = 8.27 Hz, 6H), 7.72 (d, J = 1.29 Hz, 3H), 8.24–8.35 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 20.37, 20.44, 31.6, 34.5, 56.4, 88.8, 91.3, 119.6, 123.9, 124.5, 124.7, 125.2, 125.4, 125.5, 125.8, 126.5, 127.0, 127.37, 127.44, 128.6, 129.3, 129.6, 129.8, 130.27, 130.35, 130.8, 130.9, 133.9, 134.4, 136.5, 136.9, 138.2, 138.3, 150.6, 150.7. IR (NaCl, cm^{-1}) 3064w, 2964s, 2865w, 2246vw ($\nu_{C\equiv C}$), 2038vs ($\nu_{C=N2}$), 1654m, 1577w, 1559w, 1477w, 1457w, 1438w, 1362w, 1278w, 1228w, 1190w, 1129w, 1098w, 1028w, 1000w, 945m, 907s, 867w, 824w, 786w, 763m, 731s, 668w.

Preparation of Tris(ketone) (4-3O). (a) Preparation of 3-Bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl 10-(4-*t*-Butyl-2,6-dimethylphenyl)-9-anthryl Ketone (2-O): [3-bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl][10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl]methanol (250 mg, 0.33 mmol), manganese(IV) oxide (295 mg, 3.40 mmol), and anhydrous sodium sulfate (483 mg, 3.40 mmol) were mixed in anhydrous dichloromethane (25 mL), and the mixture was stirred overnight at room temperature. The reaction mixture was filtered and the filtrated organic layer was evaporated. The crude product was chromatographed on a silica-gel column eluted with hexane/dichloromethane (2:1). 3-Bromo-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl 10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl ketone **2**-O was obtained in 89% yield (230 mg) as a yellow solid: mp 248 °C. ^{1}H NMR ($CDCl_3$): δ 1.45 (brs, 18H), 1.78 (brs, 12H), 7.27 (brs, 4H), 7.30–7.39 (m, 7H), 7.52–7.58 (m, 3H), 7.76 (s, 1H), 8.24 (d, J = 9.74 Hz, 1H), 8.27 (d, J = 9.16 Hz, 2H), 8.31 (d, J = 8.64 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 20.3, 31.5, 34.5, 120.2, 124.6, 124.8, 125.3, 125.6, 126.2, 126.9, 127.5, 127.6, 128.1, 128.3, 129.6, 129.8, 129.9, 130.3, 130.6, 130.7, 133.4, 134.1, 136.1, 136.39, 136.43, 137.0, 140.7, 141.8, 150.9, 201.7. IR (NaCl, cm^{-1}) 3063w, 2961vs, 2921m, 2865m, 1641vs ($\nu_{C=O}$), 1605w, 1559m, 1521vw, 1477s, 1442vs, 1407w, 1393vw, 1377w, 1362m, 1340vw, 1281s, 1228w, 1188m, 1128s, 1100s, 1071vw, 1028m, 998vw, 946s, 902m, 870m, 823vs, 809m, 786s, 766m, 751s, 728w, 684vw, 666m, 606vw, 583w, 557vw, 521vw. MS m/z (EI) 782 ($M+2$, 99), 780 (M^+, base). HRMS calcd for $C_{53}H_{49}BrO$, 780.2967, found m/z 780.2944 (M^+).

(b) Preparation of 10-(4-*t*-Butyl-2,6-dimethylphenyl)-9-anthryl 3-Trimethylsilylethynyl-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl Ketone (3-O(TMS)): The ketone **2**-O (100 mg, 0.13 mmol) and catalytic amounts of [$PdCl_2(Ph_3P)_2$] and copper(I) iodide were mixed with anhydrous tetrahydrofuran (1.0 mL) under nitrogen atmosphere. To this mixture, anhydrous triethylamine (0.3 mL) and trimethylsilylacetylene (0.15 mL, 0.90 mmol)

were added successively, and the mixture was stirred overnight at 40 °C. After cooling, catalysts were removed from the reaction mixture by filtration through a short alumina column (hexane). After evaporation of the solvent, the residue was purified by GPC (9 cycles, chloroform as eluent) to afford 10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl 3-trimethylsilylethynyl-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl ketone **3**-O(TMS). (69.0 mg, 66%) as a yellow solid: mp 178 °C. ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 9H), 1.45 (s, 9H), 1.46 (s, 9H), 1.76 (brs, 12H), 7.24–7.32 (m, 7H), 7.26 (s, 2H), 7.27 (s, 2H), 7.45 (dd, $J = 2.21$, 6.43 Hz, 1H), 7.52–7.55 (m, 2H), 7.69 (brs, 1H), 8.23–8.26 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 20.2, 20.3, 31.5, 34.51, 34.53, 95.9, 105.5, 120.1, 124.6, 124.7, 125.4, 125.5, 125.6, 126.0, 126.9, 127.4, 127.7, 128.98, 129.03, 129.6, 129.9, 130.0, 130.1, 130.27, 130.31, 133.8, 134.2, 136.2, 136.6, 136.7, 141.6, 141.7, 150.7, 150.9, 202.0. IR (NaCl, cm^{-1}) 3065w, 2963vs, 2867m, 2151m ($\nu_{C\equiv C}$), 1637vs ($\nu_{C=O}$), 1560m, 1477m, 1451m, 1442m, 1362m, 1282m, 1250m, 1229w, 1185m, 1128s, 1098s, 1028w, 988w, 945m, 910m, 859s, 843s, 830w, 808m, 787m, 765m, 750m, 733s, 664w. MS m/z (relative intensity) 800 (M + 2, 25.7), 799 (M + 1, 64.5), 798 (M$^+$, 100); HRMS calcd for $C_{58}H_{58}OSi$ 798.4257, found m/z 798.4275.

(c) Preparation of 3-Ethynyl-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl 10-(4-*t*-Butyl-2,6-dimethylphenyl)-9-anthryl Ketone (3-O): To a solution of the ketone **3**-O(TMS) (69.0 mg, 0.086 mmol) in *t*-butyl alcohol (12 mL) was added 10% aqueous solution (4 mL) of sodium hydroxide, and the mixture was stirred overnight at room temperature. The reaction mixture was extracted with diethyl ether, and organic layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by GPC (7 cycles, chloroform as eluent) to afford 3-ethynyl-10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl 10-(4-*t*-butyl-2,6-dimethylphenyl)-9-anthryl ketone **3**-O (62 mg, quantitatively) as a yellow viscous liquid. ^{1}H NMR ($CDCl_3$): δ 1.45 (brs, 18H), 1.76 (brs, 12H), 3.08 (s, 1H), 7.26–7.31 (m, 11H), 7.48–7.55 (m, 3H), 7.73 (d, $J = 1.47$ Hz, 1H), 8.22–8.26 (m, 4H). IR (NaCl, cm^{-1}) 1637vs ($\nu_{C=O}$).

(d) Preparation of Tris(ketone) (4-3O): The ketone **3**-O (55.2 mg, 0.076 mmol), 1,3,5-triiodobenzene (10.0 mg, 0.025 mmol) and catalytic amounts of [$PdCl_2(Ph_3P)_2$] and copper(I) iodide were mixed with anhydrous tetrahydrofuran (0.8 mL) under nitrogen atmosphere. To this mixture, anhydrous triethylamine (0.3 mL) was added and the mixture was stirred overnight at room temperature. Removal of the catalyst by filtration through a short alumina column, followed by removal of the solvent, gave crude material which was purified by GPC (8 cycles, chloroform as eluent) to give tri(ketone) compound **4**-3O (26.0 mg, 46%) as a yellow solid: mp 279 °C. ^{1}H NMR ($CDCl_3$): δ 1.45 (brs, 54H), 1.77 (brs, 36H), 7.25–7.33 (m, 33H), 7.47 (dd, $J = 2.85$, 7.07 Hz, 3H), 7.55 (s, 3H), 7.56 (dd, $J = 3.12$, 7.12 Hz, 6H), 7.71 (d, $J = 1.10$ Hz, 3H), 8.23–8.28 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 20.3, 31.5, 34.5, 88.9, 91.1, 119.7, 123.8, 124.6, 124.8, 125.4, 125.6, 125.8, 126.0, 126.9, 127.4, 127.8, 129.0, 129.4, 129.6, 129.9, 130.2, 130.4, 133.7, 134.2, 136.2, 136.5, 136.7, 141.7, 150.8, 201.9. IR (NaCl, cm^{-1}) 3062w, 3012w, 2965vs, 2916m, 2866w, 2211w ($\nu_{C\equiv C}$), 1641vs ($\nu_{C=C}$), 1607m, 1579m, 1559m, 1521w, 1478m, 1442m, 1407w, 1378w, 1362m, 1282s, 1216m, 1190m, 1129s, 1098s, 1028w, 1000w, 945m, 869m, 827s, 813w, 787s, 757vs, 668w. MS m/z (relative intensity) 2255 (M + 4, 33), 2254 (M + 3, 57), 2253 (M + 2, 85), 2252 (M + 1, 100), 2251 (M$^+$, 62); HRMS calcd for $C_{171}H_{150}O_3$ 2251.1580, found m/z 2251.1432.

ESR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (10^{-3} M) and the solution was degassed in a quartz cell by three freeze–degas–thaw cycles. The sample was cooled in an optical transmission ESR cavity at 77 K and irradiated with a Wacom 500 W Xe lamp using a Pyrex filter. ESR spectra were measured on a JEOL JES TE 200 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gaussmeter. The temperature was controlled by a 9650 Microprocessor-based Digital Temperature Indicator/Controller, which provided the measurement accuracy within ±0.1 K and the control ability within ±0.2 K. Errors in the measurements of component amplitudes did not exceed 5%; the accuracy of the resonance fields determination was within ±0.5 mT.

Low-Temperature UV–Vis Spectra. Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN 1704) equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF, placed in a long-necked quartz cuvette of 1-mm path length, and degassed thoroughly by repeated freeze–degas–thaw cycles at a pressure near 10^{-5} Torr. The cuvette was flame-sealed under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Halos 300-W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC 4).

Flash Photolysis. All flash measurements were made on a Unisoku TSP-601 flash spectrometer. Three excitation light sources were used, depending on the precursor absorption bands and lifetime of the transient species. They were (i) a cylindrical 150-W Xe flash lamp (100 J/flash with 10-ms pulse duration); (ii) a Quanta-Ray GCR-11 Nd:YAG laser (355 nm pulses of up to 40 mJ/pulse and 5–6-ns duration; 266 nm pulses of up to 30 mJ/pulse and 4–5-ns duration); and (iii) Lamda Physik LEXTRA XeCl excimer laser (308 nm pulses of up to 200 mJ/pulse and 17-ns duration). The beam shape and size were controlled by a focal length cylindrical lens.

A Hamamatsu 150-W xenon short arc lamp (L 2195) was used as the probe source, and the monitoring beam, guided using an optical fiber scope, was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q MOS linear image sensor (512 photodiodes used). Timing of the excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu Model DS-8631 digital synchro scope which was interfaced to a NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphic capabilities. Each trace was also displayed on a NEC CRT N5913U monitor.

A sample was placed in a long-necked Pyrex tube which had a side arm connected to a quartz fluorescence cuvette and degassed using a minimum of four freeze–degas–thaw cycles at a pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was flame-sealed under reduced pressure, and the solution was transferred to the quartz cuvette, which was placed in the sample chamber of the flash spectrometer. A cell holder block of the sample chamber was equipped with a thermostat and allowed to come to thermal equilibrium. The concentration of the sample was adjusted so that it absorbed a significant portion of the excitation light.

SQUID Measurements. Magnetic susceptibility data were obtained on a quantum design MPMS-2A superconducting quantum interference device (SQUID) magnetometer/susceptometer. Irradiation with light from an argon ion laser (488 nm, Omnichrome 543-150BS) through a flexible optical fiber which passes through the inside of the SQUID sample holder was performed inside the sample room of SQUID apparatus at 5–11 K. One end of the optical fiber was located 40 mm above the sample cell (capsule) and the other was attached to a coupler for the laser. The bottom part of the capsule (6×10 mm^2) without a cap was used as a sample cell. A 50 μL portion of the sample solution (0.5 mM) in 2-MTHF was placed in the cell which was held by a straw. The irradiation was carried out until there is no further change of magnetization monitored at 5 K in a constant field of 5 kOe. The magnetization, Mb and Ma, before and after irradiation was measured at 5 K in a field range 0–50 kOe. The plots of the magnetization [$M = (M\mathrm{a} - M\mathrm{b})$: F stands for a photolysis factor of diazo compound] versus the magnetic field were analyzed in terms of Brillouin functions.

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Supporting Information

MALDI-TOF MS spectra of the tris(ketone) (Fig. S1); GPC chart of tris(diazo) and tris(ketone) compounds (Fig. S2); Simulated ESR spectra of tris(carbene) (Fig. S3); MALDI-TOF MS spectra of the spent solution of LFP of mono(diazo) and tris(diazo) compounds (Figs. S4 and S5); ESR spectra obtained after irradiation of tris(diazo) compound (Fig. S6). This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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