Supporting Information

Preparation of Poly(phenyl)acetylenes Having Diazo Groups and Magnetic Characterization of Poly(carbene)

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Experimental Section

General. Reagent were obtained commercially and used without further purification unless otherwise noted. Tetrahydrofuran, ether, toluene and dioxane were dried by benzophenone ketyl (sodium/benzophenon) and dichloromethane, carbon tetrachloride and triethylamine were dried by calcium hydride. IR spectra were measured on a JASCO FT/IR-410 spectrometer, and UV-vis spectra were recorded on a JASCO V-560 spectrometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer and Applied Biosystems VoyagerDE-Pro(MALDI-TOF-MS). ^{1}H and ^{13}C NMR spectra were determined with JEOL JNM-AL300 FT/NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. The magnetic measurements were done on a 5-T Quantum Design MPMS SQUID magnetometer. Thin-layer chromatography was done on Merck Kieselgel 60 PF_{254}. Column chromatograph was carried out on a silica gel (Merck for dry column chromatography) or on an aluminum oxide, active neutral (activity I) (ICN for column chromatography). GPC was undertaken with

a JASCO PU-986 chromatograph with a UV-970 UV/vis detector using a Shodex GPC H-2001 (20 mm × 50 cm) or GPC H-2002.5 (20 mm × 50 cm). Molecular weights of Polymer were determined by GPC calibrated with polystyrene standard and equipped analytical gel column, Shodex GPC K-804L (8 mm × 30 cm).

Diazo compounds should be treated as highly toxic and potentially explosive. Although the diaryldiazomethanesand poly(diazo) compounds employed in this report is relatively insensitive to heat and shock, all procedures should be routinely carried out behind a safety shield.

Preparation of Poly(diazo) Compound (3-nN_2). A solution of [Rh(norbornadiene)Cl]$_2$ (1 mg, 0.002 mmol) and absolute triethylamine (2 ml) in absolute toluene (20 ml) was added to a stirred solution of (2,6-dibromo-4-ethynylphenyl)(4-*tert*-butyl-2,6-dimethylphenyl)-diazomethane (2-N_2) in absolute toluene (50 ml). After stirring at room temperature for one day, the reaction mixture was poured into MeOH to terminate the polymerization. The resulting precipitate was filtered, washed with MeOH and dried in vacuum. The crude product was purified by repeated chromatography on a gel permeation column with $CHCl_3$ (Figure S1). Poly(diazo) compound (3-nN_2) was obtained as red solid in 7% yield: M=86,000 (ca. 190 mer); IR (NaCl) 2066 cm^{-1} (Figure S2).^{1}HNMR($CDCl_3$) (Figure S3) 1.25 (bs), 2.17 (bs), 5.93 (bs), 7.00 (bs) and 7.34 (bs).

It is not possible to obtain elemental analysis and MS data as diazo functional groups are usually not stable enough to survive elemental analysis procedures and mass measurements. Sometimes a diazo compound could be converted to a stable compound from which we could obtain mass data, but those sterically congested diazo compounds result in the formation of rather complex product mixtures upon such conversion reactions. Thus it is not possible to estimate how much of the diazo functional groups are retained during polymerization by mass measurements. However it is likely that "most" of diazo groups are intact during the polymerization as the intensities of diazo band at 2066 cm^{-1} relative to other bands in polydiazo compound **3**-nN_2 are very similar with those in monomer **2**-N_2 (Figure S2) and that NMR signals of polydiazo compound **3**-nN_2 are mostly from that expected from one unit structure.

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 mm x 10 mm) without a cap was used as a sample cell. A 50 μL of the sample solution (0.5 mM) in 2-methyltetrahydrofuran 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 [$M = (M_b\text{-}M_a)$: F stands for a photolysis factor of diazo compound] *versus* the magnetic field were analyzed in terms of Brillouin function equation 1. More explicitly, S value is estimated from the curvature of the plot while F is obtained by matching the curve to the vertical axis.

The IR measurements were made before and after irradiation to identify the fraction of diazo groups photolyzed in the magnetic measurements. However experimental errors in analyzing small quantity (0.05 mL) of very dilute (0.5 mM) were rather significant in this analysis.

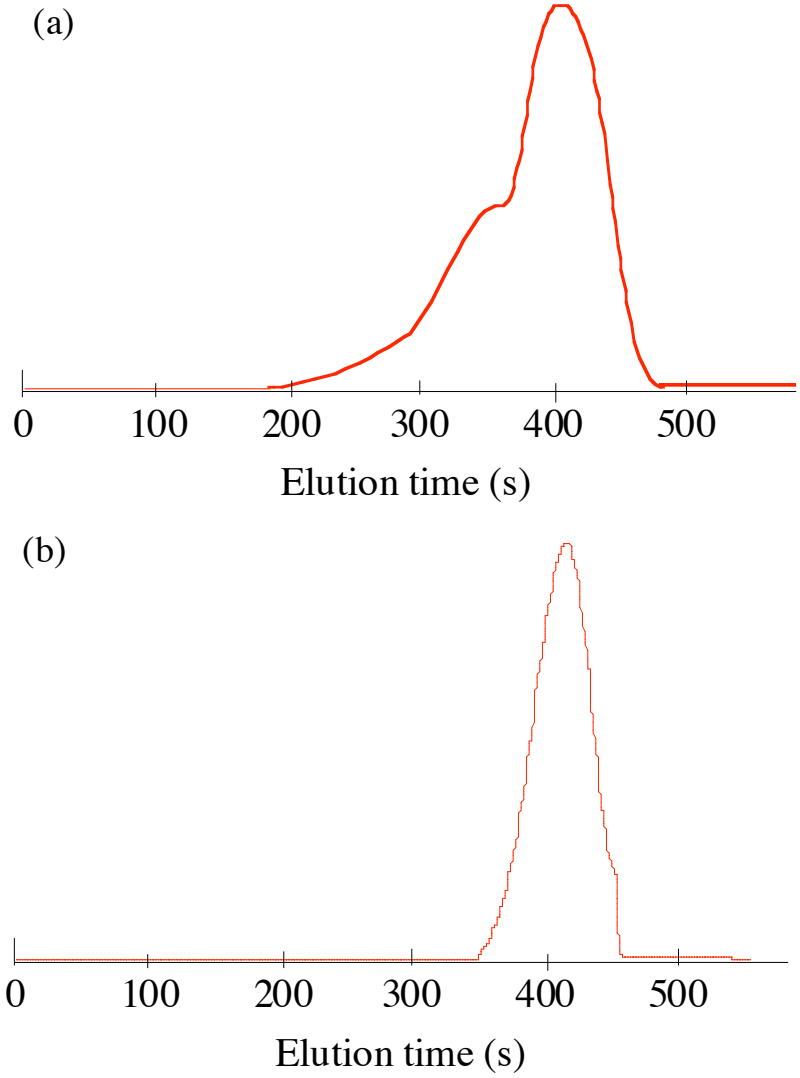

Figure S1. (a) GPC chart of a crude poly(diazo) compound **3**-nN_2 and (b) GPC chart of purified poly(diazo) compound **3**-nN_2.Column :Shodex GPC K-804L, flow rate: 1.0mL/min, solvent:$CHCl_3$, Monitor wavelength: 280 nm.

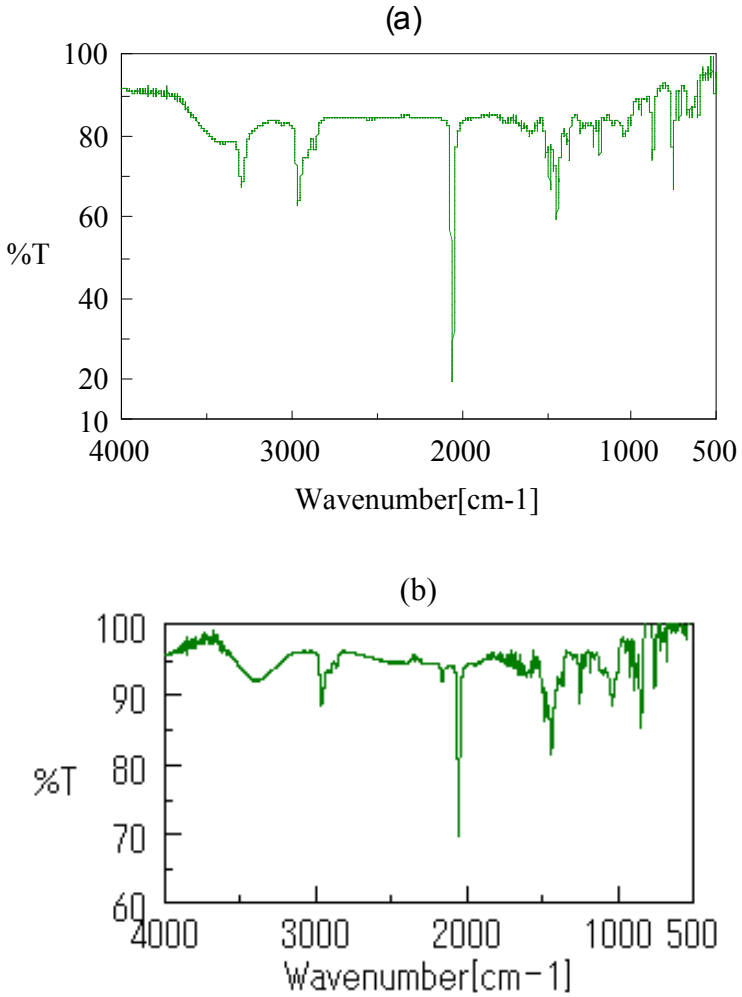

Figure S2. IR chart of (a) the starting diazo compound **2**-N_2 and (b) purified poly(diazo) compound **3**-nN_2.

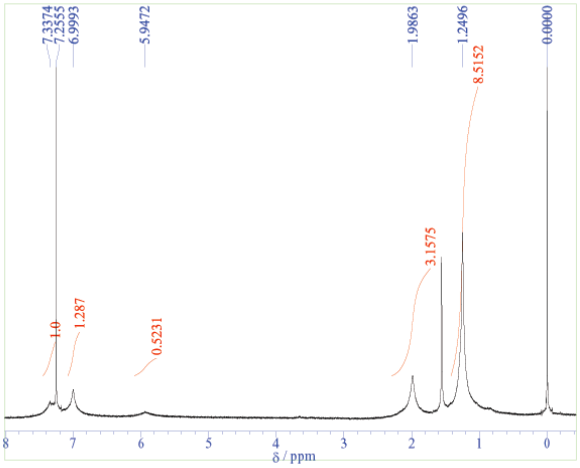

Figure S3. ^{1}HNMR chart of poly(diazo) compound **3**-nN_2.

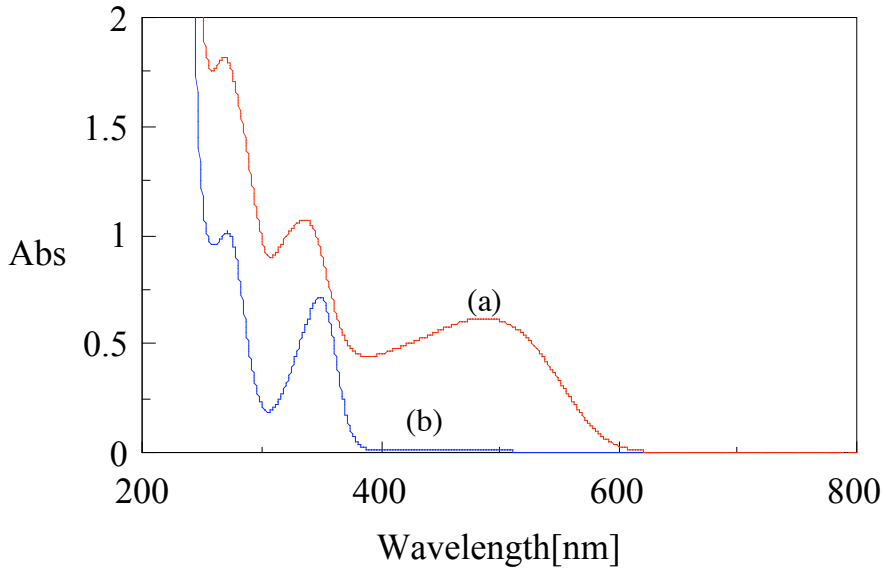

Figure S4. UV/vis chart of (a) purified poly(diazo) compound **3**-nN_2 and (b) the starting diazo compound **2**-N_2

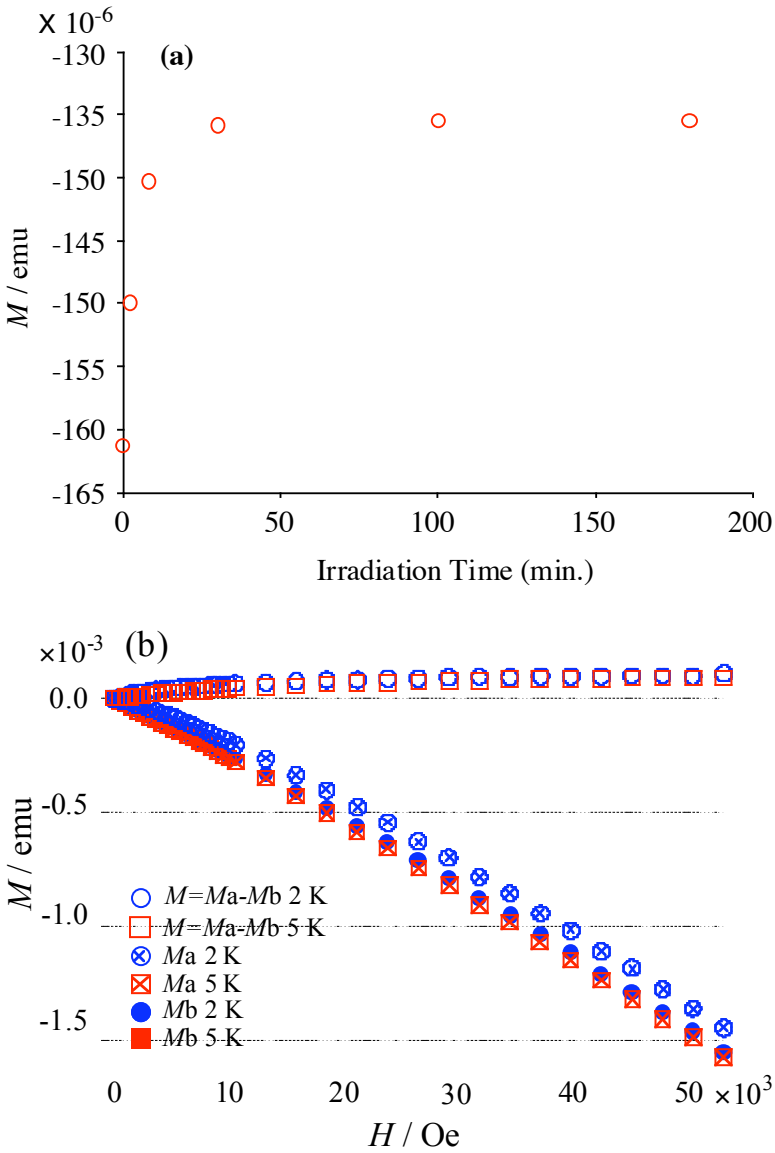

Figure S5. (a) Plot of magnetization (M in emu) as a function of irradiation time observed in the photolysis of poly(diazo) compound **3**-nN_2 in 0.10 mM 2-methyltetrahydrofuran matrix measured at 5.0 K and 5 kOe. (b) Field dependence of the magnetization of the photoproduct from poly(diazo) compound **3**-nN_2 in 0.10 mM 2-methyltetrahydrofuran matrix measured at 2.0 and 5.0 K. M_a and M_b refer to the magnetization value before and after irradiation, respectively, and $M = M_b$-M_a.