Supporting Information

A High-spin s-Trazine Linked Fluorenyl Radical Polymer

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ABSTRACT: Syntheses of high-spin organic polymers have been a daunting task due to the highly reactive nature of organic radicals, especially when they are ferromagnetically coupled. In this paper, we report our approach to obtain high-spin organic polymers, in which reasonably stable fluorenyl radical was employed as the primary radical unit, and s-triazine serves as the connector that facilitates ferromagnetically coupling between them. The diamagnetic polymer precursor was synthesized by cyclotrimerization of a cyano-monomer, and the high-spin polymers were obtained by oxidizing corresponding anionic polymers using O_2 (**6**) or I_2 (**7**). The temperature-dependent magnetic moments, and field-dependent magnetization data obtained from SQUID measurements suggested ferromagnetic couplings between primary radical units with coupling J = 7.5 cm^{-1} and 38.6 cm^{-1}, and the percentage of primary unit in the radical form are 29%, and 47% for **6** and **7**, respectively. This is the first time a high-spin ferromagnetically coupled fluorenyl radical polymer has ever been reported.

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General Experimental Procedures

Magnetic measurements. ESR spectra of the as-formed solid samples were recorded on a X-band spectrometer (9.5 GHz), JES-FA100 (JEOL) with a microwave power of 1 mW, a field modulation frequency of 100 kHz, and a modulation amplitude of 0.4 G. A Quantum Design 7 Tesla SQUID VSM system was available for the magnetic susceptibility measurements in this work. Powder sample with a weight of 5-10 mg was sealed in a plastic capsule. The magnetic susceptibility was measured in the temperature range of 2 to 30 K with an applied field of 10 Oe, or 1000 Oe. Field dependent magnetization was obtained at 2K (0 – 5 T), 10 K, 100 K, 200 K, 300 K (0 – 2 T). Then, the data were corrected diamagnetic contribution from sample holders and sample themselves using tabulated constants. The high-temperature part of the temperature-dependent $1/\chi_{unit}$ of the sample **6, 7** was fitted by using Curie-Weiss law:

$$\frac{1}{\chi_{unit}} = \frac{T - \theta}{C}$$

where C is the Curie constant and θ is the Weiss constant:

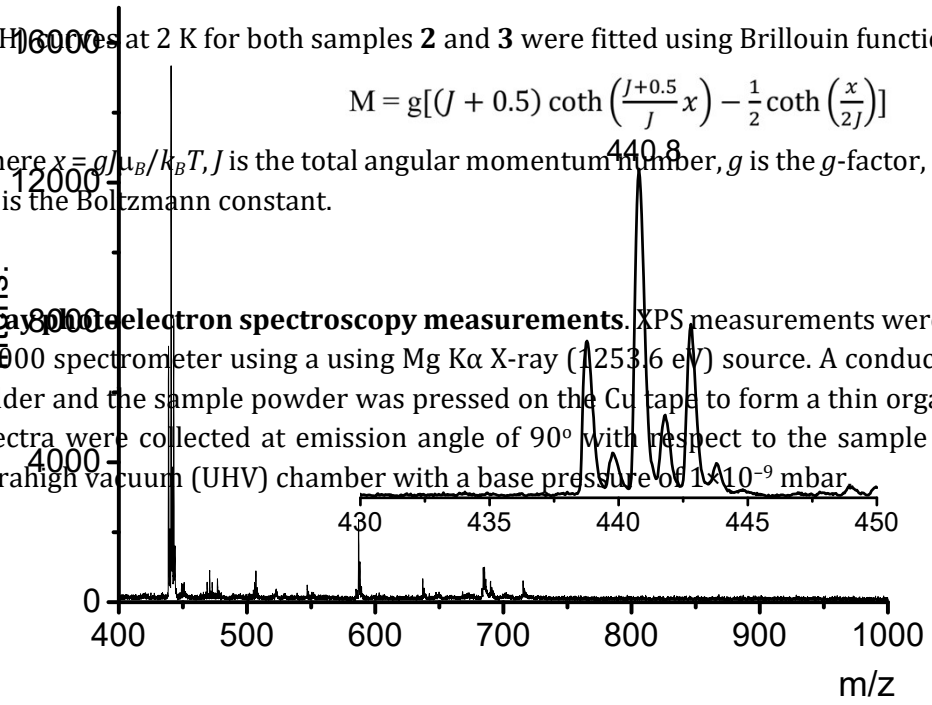
$$\theta = \frac{2zJS(S+1)}{3k_B}$$

where z is the number of nearest neighbors around each radical anion, z = 3 for this case.

M(H) curves at 2 K for both samples **2** and **3** were fitted using Brillouin function:

$$\mathrm{M} = \mathrm{g}[(J + 0.5)\coth\left(\frac{J+0.5}{J}x\right) - \frac{1}{2}\coth\left(\frac{x}{2J}\right)]$$

Where $x = gJ\mu_B/k_BT$, J is the total angular momentum number, g is the g-factor, μB is the Bohr magneton and kB is the Boltzmann constant.



X-ray photoelectron spectroscopy measurements. XPS measurements were performed on a VG Scienta-R4000 spectrometer using a using Mg Kα X-ray (1253.6 eV) source. A conductive Cu tape was attached to holder and the sample powder was pressed on the Cu tape to form a thin organic layer. All photoemission spectra were collected at emission angle of 90° with respect to the sample surface, and operated in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-9} mbar.

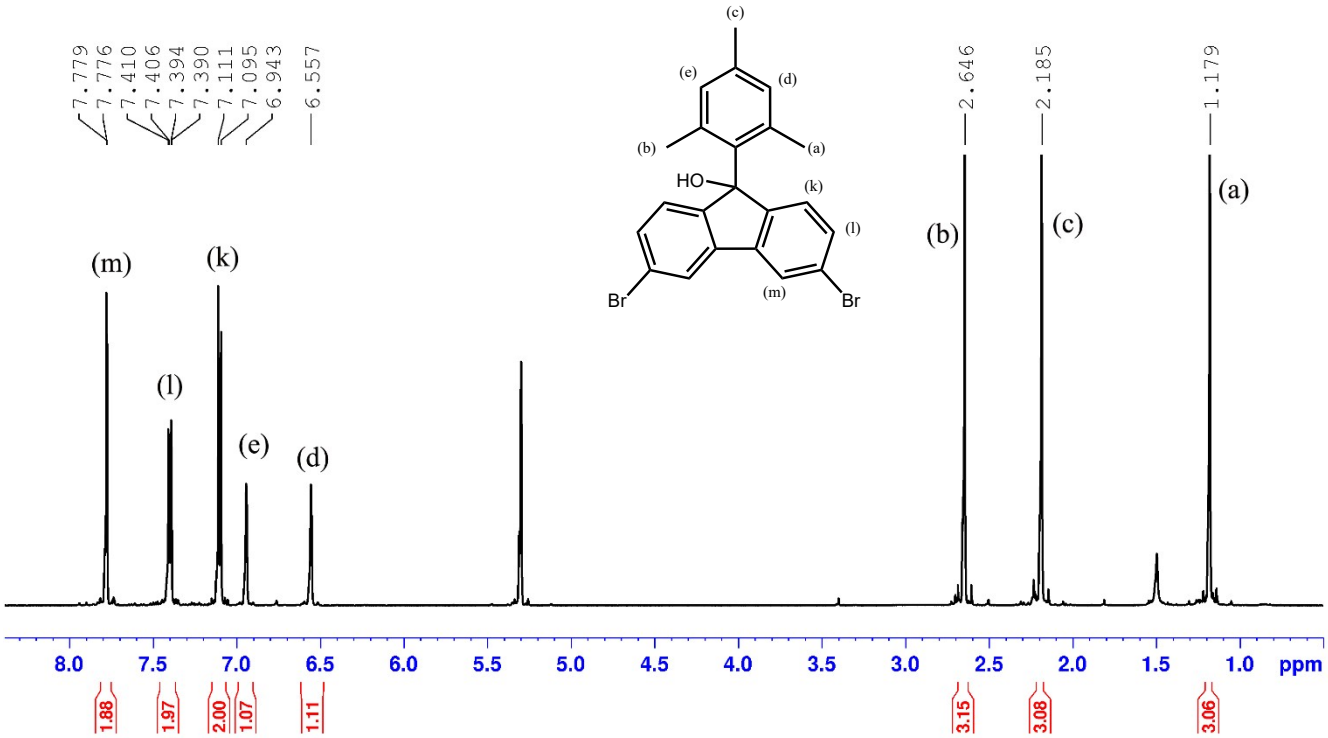
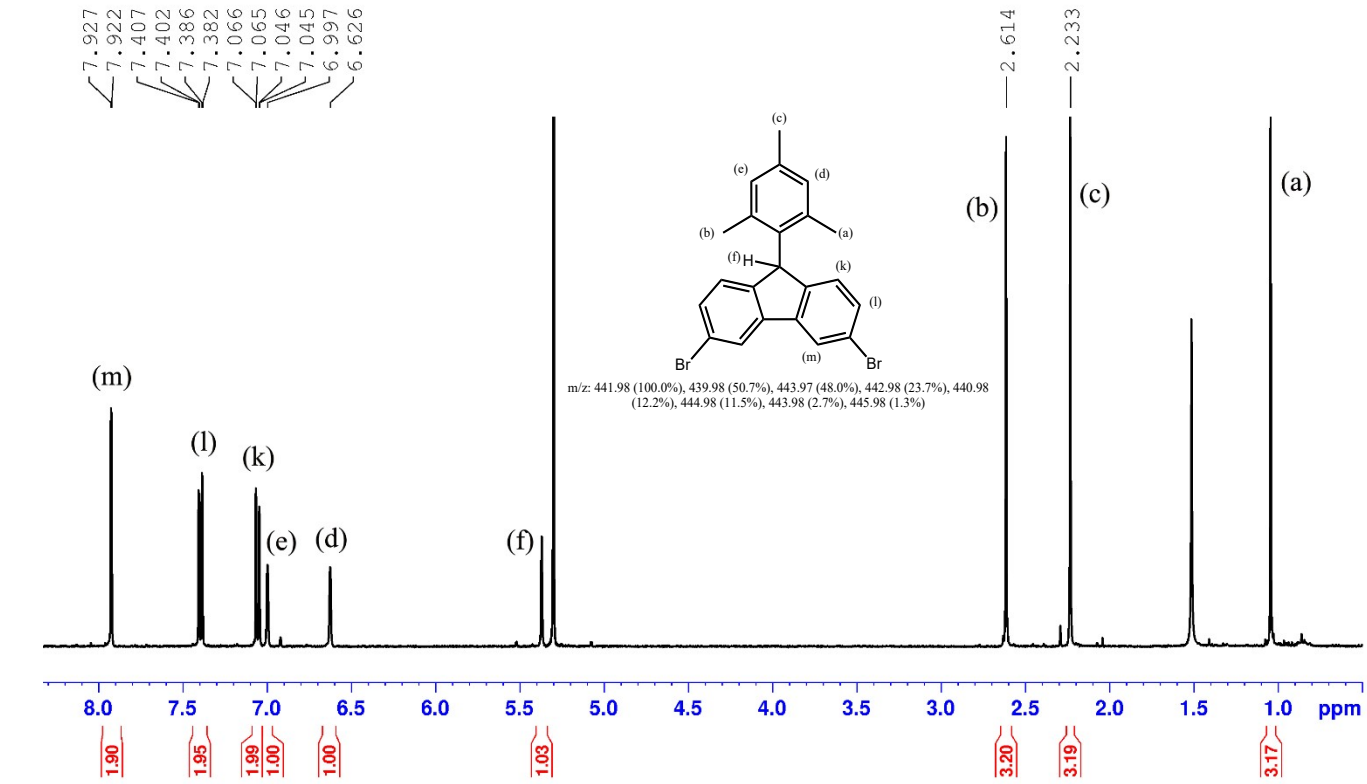


Figure S1. ^{1}H NMR spectrum of **1**



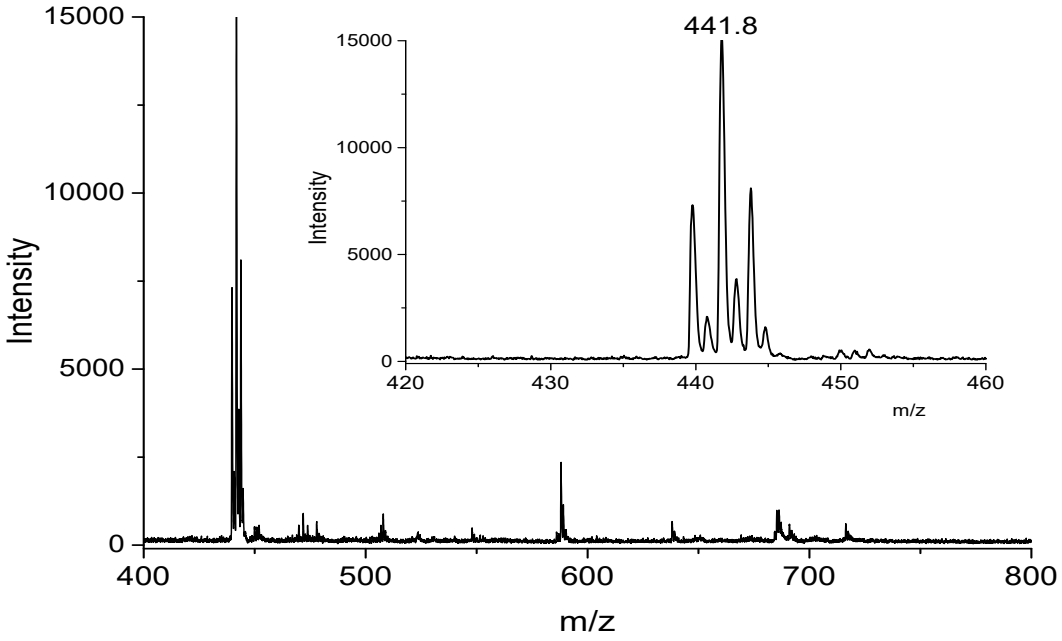


Figure S2. ^{1}H NMR spectrum (top) and MALDI-TOF (bottom) (the inset: zoom in at molecular peaks) of **2.**

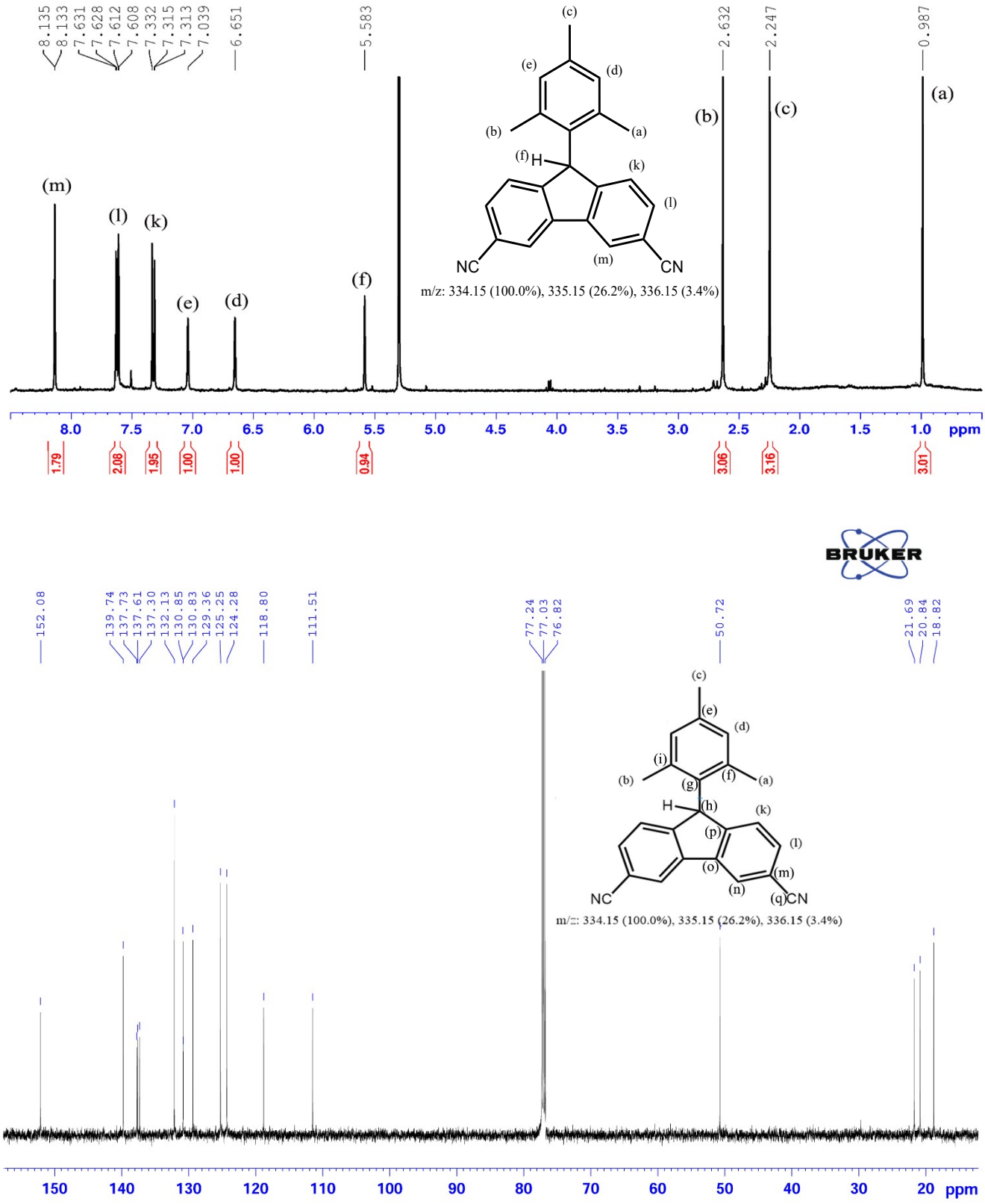


Figure S3. ^{1}H NMR spectrum (top) and ^{13}C NMR (bottom) of compound **3**.

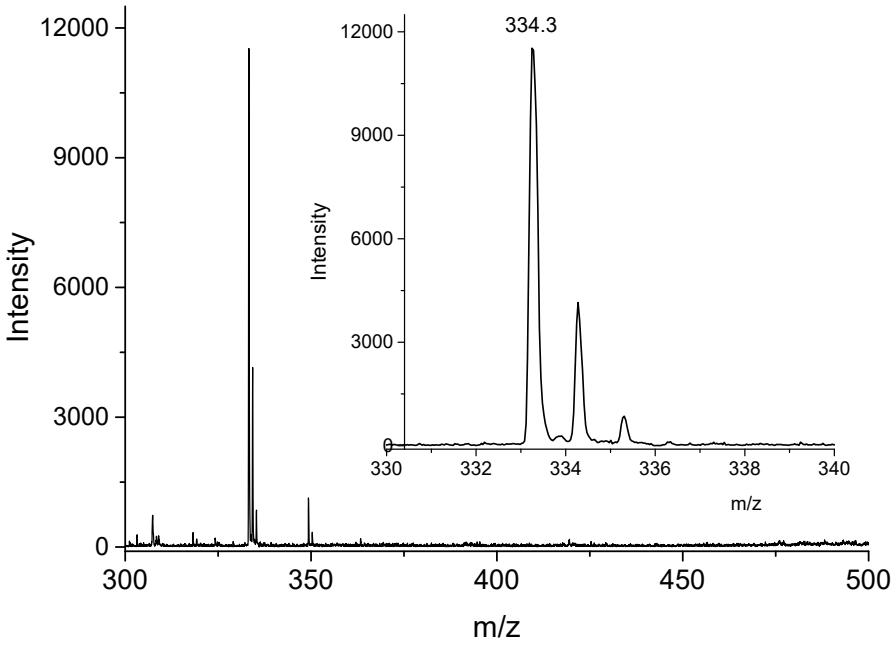


Figure S4. MALDI-TOF (the inset: zoom in at molecular peaks) of **3.**

DFT calculations

Density functional theory calculations were employed with Orca 4.0 package [1,2], utilizing the B3LYP function and 6-31G basis set [9, 10] for the molecules with 21 and 45 primary fluorenyl units.

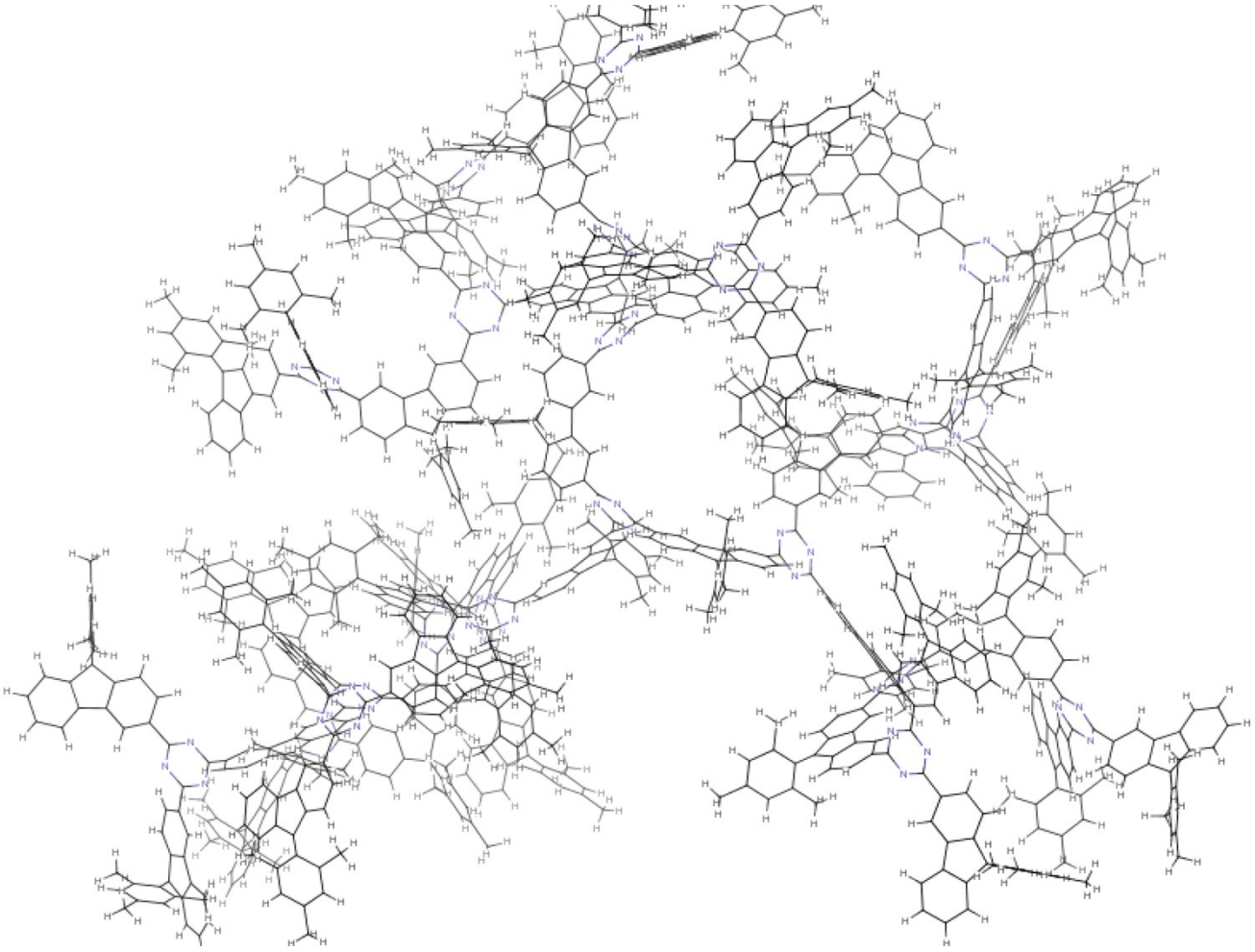


Figure S5. Optimized molecular struture with 45 primary units.

The singlet and triplet states of the dimer density functional theory calculations were employed with Gaussian 09 package,[11] utilizing the UCAM-B3LYP[12-14] level of theory with Pople basis set 6-31G*[15-17] for all molecules in the gas phase.

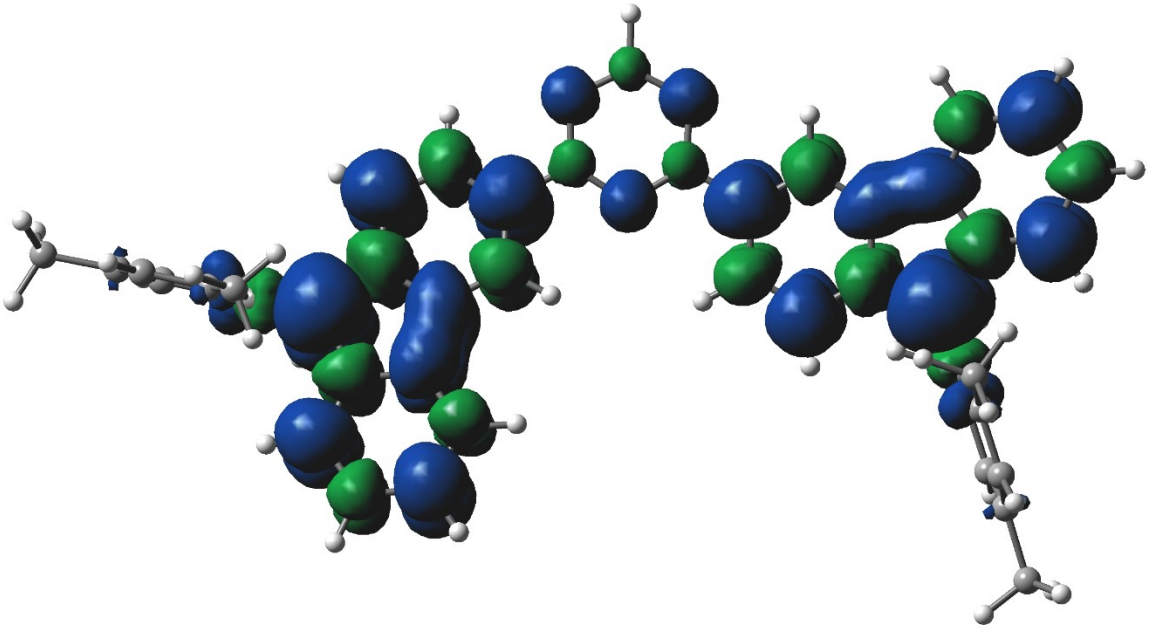


Figure S6. Spin density of the dimer.

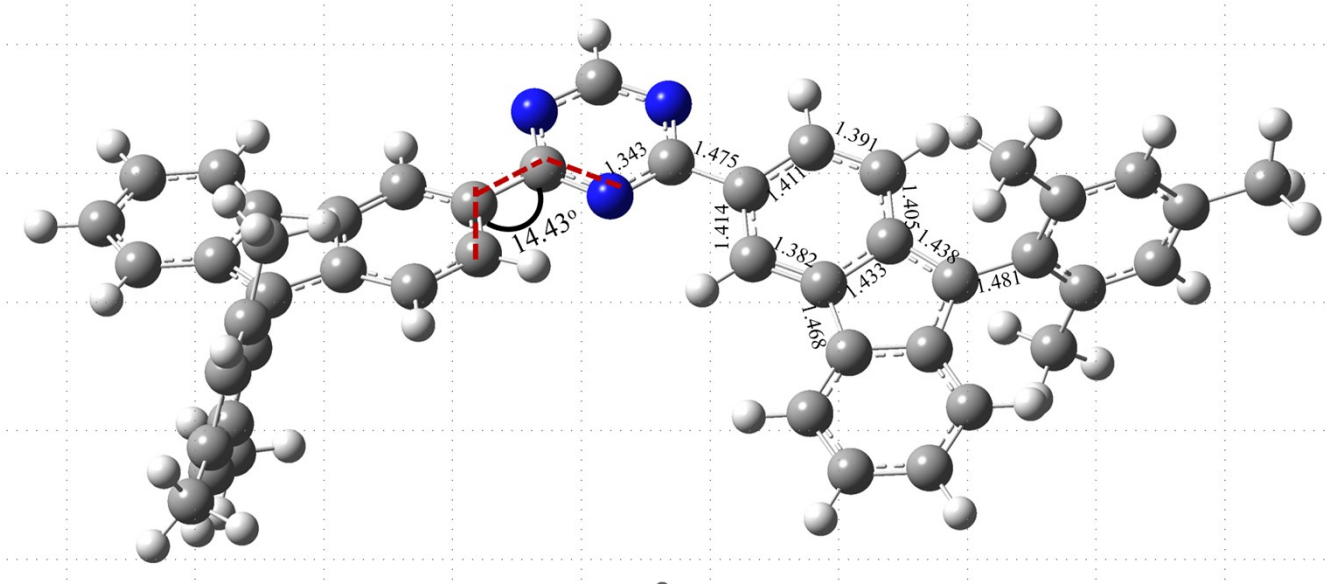


Figure S7. The dihedral angle between the radical and s-triazine moiety and some calculated C-C bond lengths (in Å) in the triplet ground state.

Singlet state

```
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 \C,0,-36.3965,33.0652,-42.4825\C,0,-35.0556,33.2377,-42.832\C,0,-34.24
```

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,0,-36.5563,29.6495,-42.3139\C,0,-32.5418,30.5795,-43.3842\C,0,-31.340
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Triplet state

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2\C,0,-31.3407,29.9075,-43.6654\C,0,-31.3147,28.5174,-43.6173\C,0,-33.

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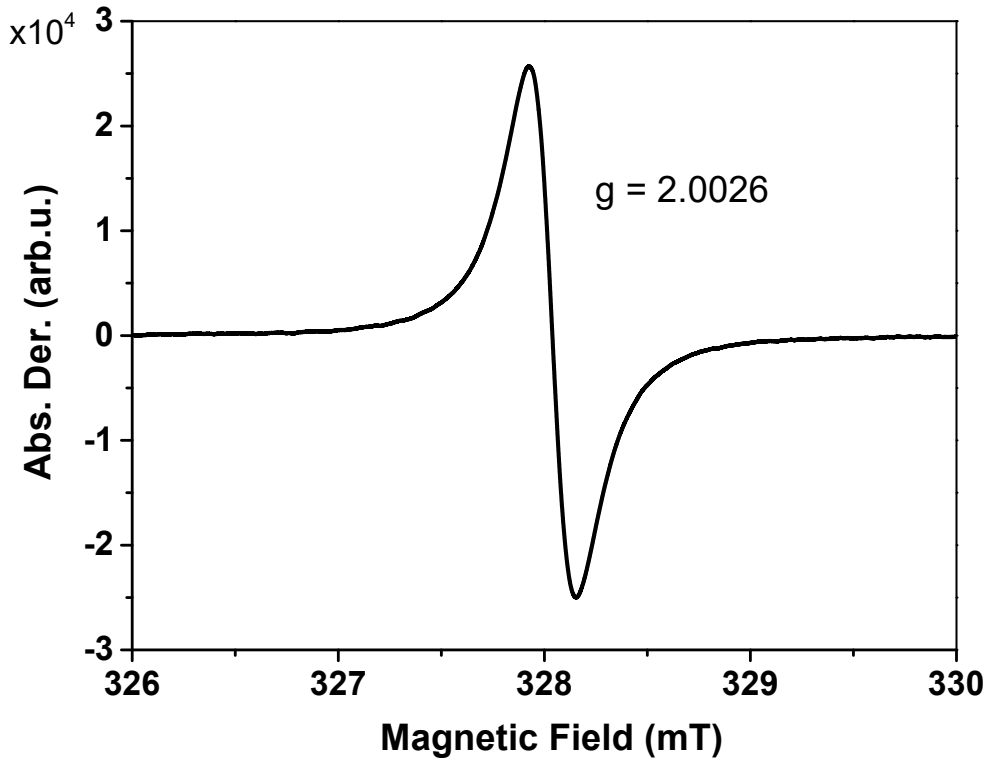

Figure S8. Solid state ESR spectrum of compound **7**, recorded at ambient conditions.

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Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2009.

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