

Supporting Information (SI)

Synthesis and Characterization of 1,1'-Azobis(5-methyltetrazole)

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Experimental Section

Caution: 1,1'-azobis(5-methyltetrazole) reported in this publication is very sensitive towards friction, impact, and electrostatic discharge. Therefore proper safety precautions should be taken when handling these compounds. Laboratories and personnel should be properly grounded, and safety equipment such as Kevlar gloves, leather coats, face shields, and ear plugs are recommended.

General methods: All chemical reagents and solvents (analytical grade) were used as supplied unless otherwise stated. ^1H and ^{13}C spectra were measured with a Bruker Avance III 500 MHz Digital NMR Spectrometer operating at 500, 126 MHz. All chemical shifts are quoted in ppm relative to TMS (^1H , ^{13}C). FT-IR spectra was recorded on a BOMEM MB Series 154S FTIR spectrometer. Raman spectra was measured with a RamTracer®-200 instrument. Mass spectra was recorded on Finnigan TSQ Quantum ultra instrument using electro spray ionization (ESI) method. Elemental analysis was performed by on a Vario EL III recorder. TG and DSC studies were carried out on a STD-Q600 at a heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in closed Al containers with a nitrogen flow of $80\text{ mL}\cdot\text{min}^{-1}$ (0.162 mg of powder). The electrostatic sensitivity test was carried out using an Electric Spark Tester ESD JGY-50 III.

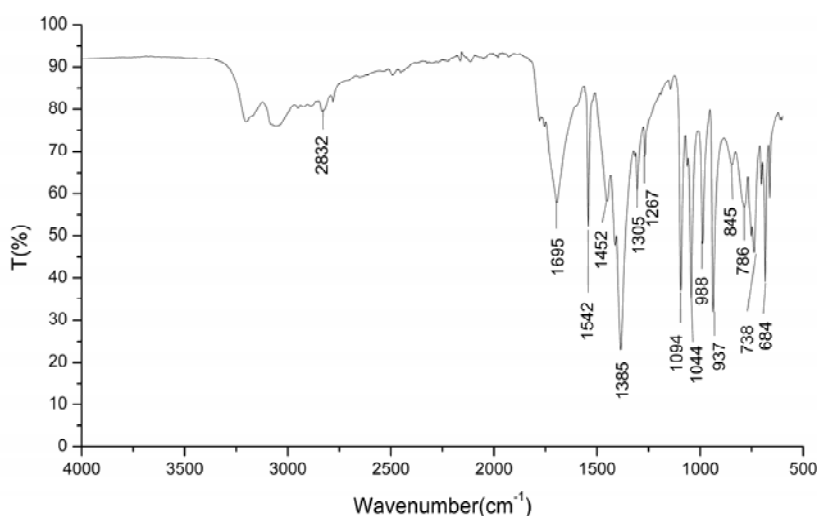


Figure S1. Infrared spectrum of 5

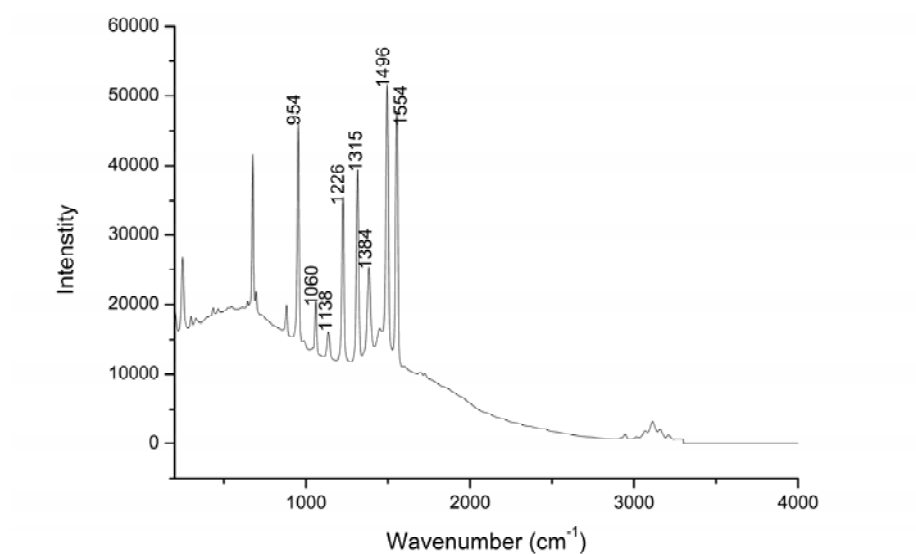


Figure S2. Raman spectrum of **5**

Table S1. Selected Raman and IR frequencies for **5** presented and their possible assignment.

IR	Raman	Possible assignment
2832	--	$\nu_s\text{CH}_3$
1542	1554	$\nu(\text{C}_1=\text{N}_1+\text{N}_5=\text{N}_6)$
1452	1496	$\nu_{\text{as}}(\text{N}_1=\text{C}_1-\text{N}_4) + \delta_{\text{as}}\text{CH}_3$
1385	1384	$\nu(\text{N}_2=\text{N}_3), \delta_s\text{CH}_3$
1305	1315	$\nu(\text{C}_1=\text{N}_1), \nu(\text{N}_2=\text{N}_3)$
1267	1226	$\nu_{\text{as}}(\text{N}_5-\text{N}_4-\text{N}_3)$
1094	1138	$\nu_{\text{as}}(\text{N}_1-\text{N}_2+\text{N}_3-\text{N}_4)$
1044	1060	$\nu_s(\text{N}_1-\text{N}_2+\text{N}_3-\text{N}_4)$

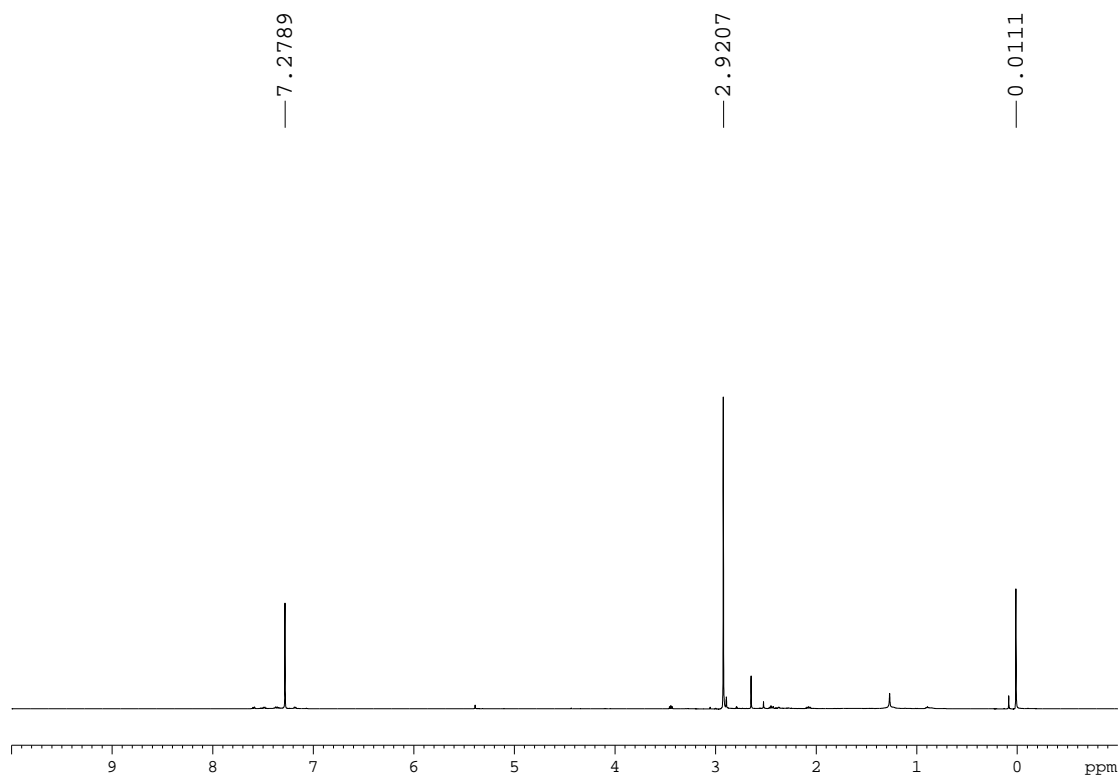


Figure S3. ^1H NMR spectrum (500 MHz) of **5** in CDCl_3 at 25 $^\circ\text{C}$

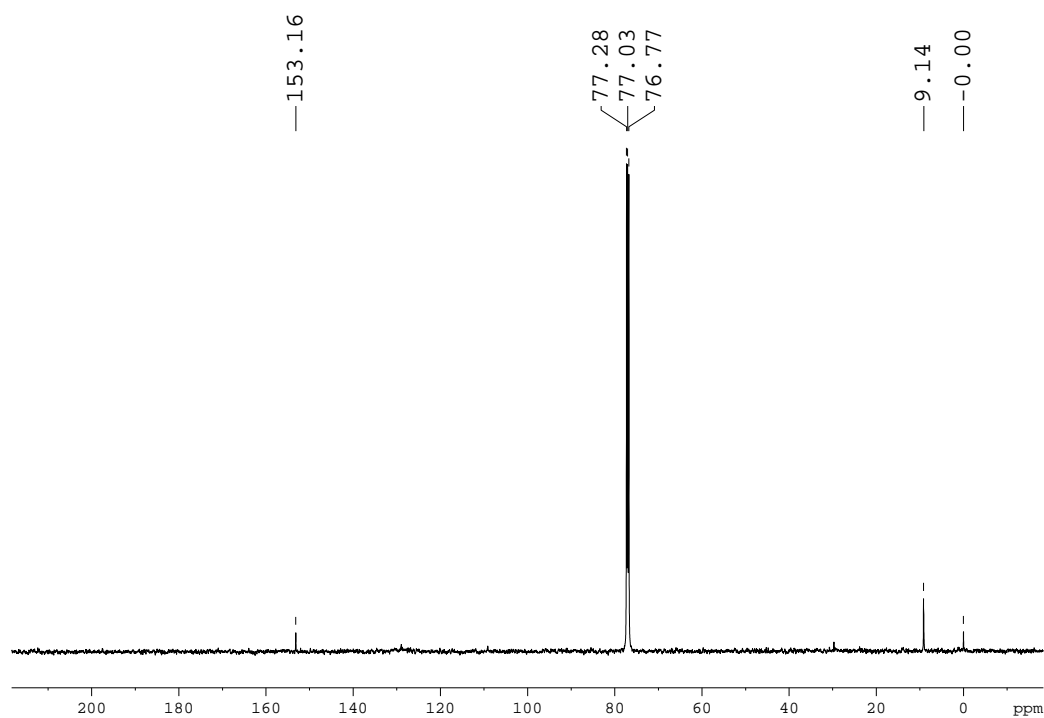


Figure S4. ^{13}C NMR spectrum (126 MHz) of **5** in CDCl_3 at 25 $^\circ\text{C}$

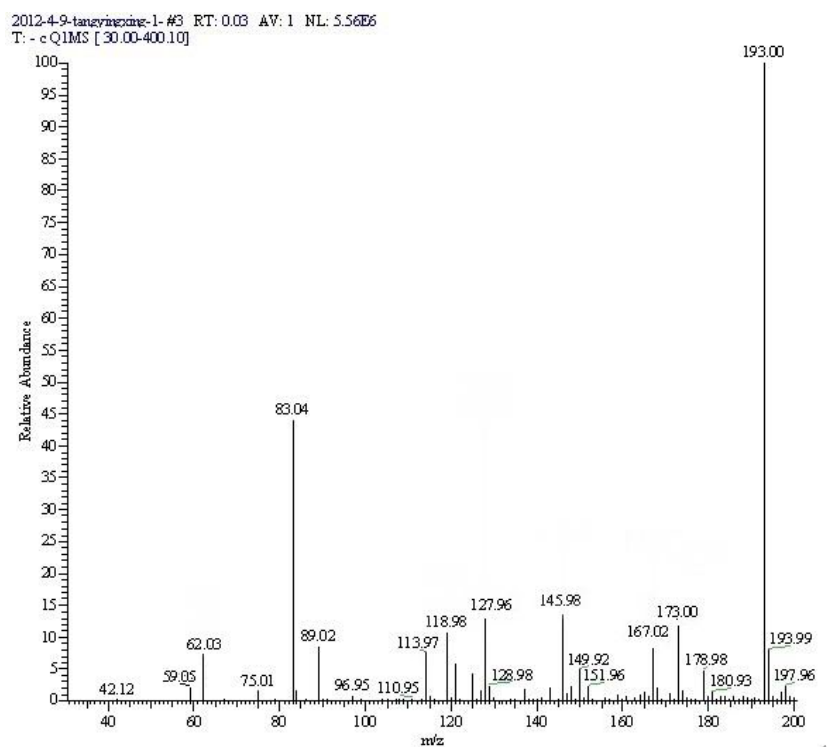


Figure S5. Mass spectrum of **5**

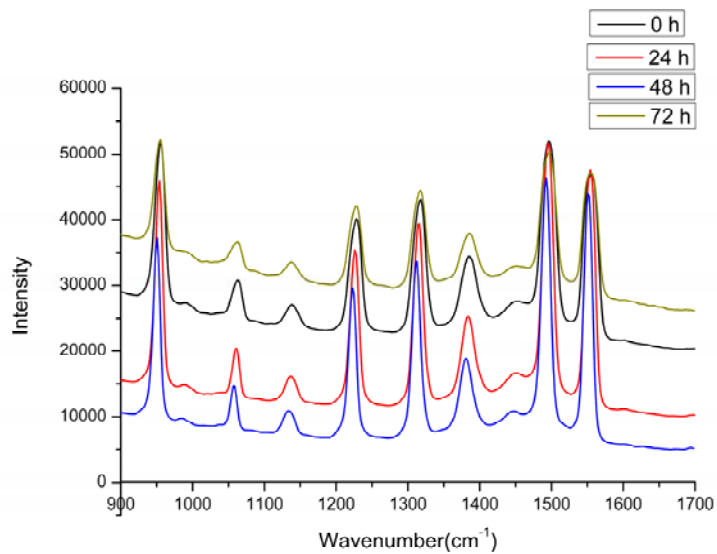


Figure S6. No change at Raman spectrum of **5** upon influence of UV light for the three days

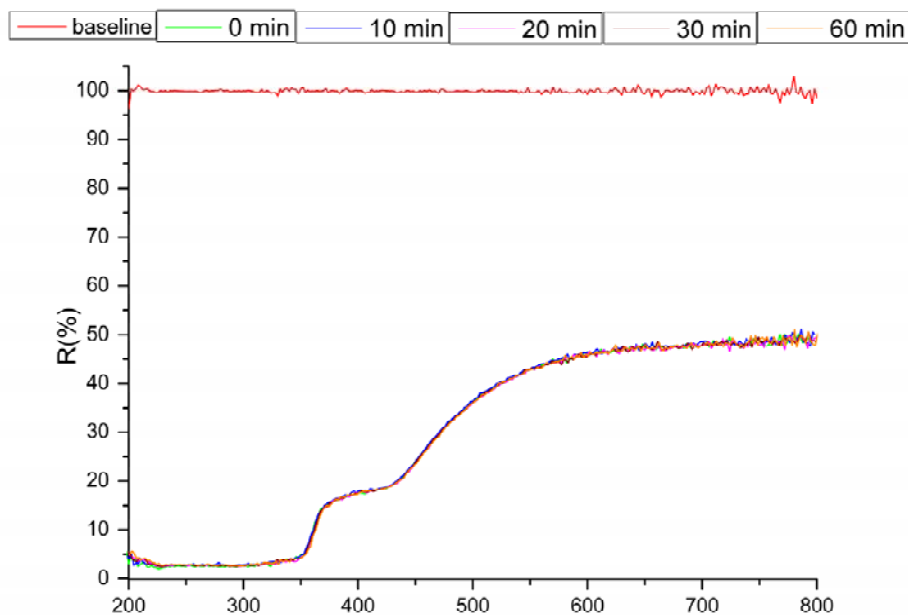


Figure S7. No change at UV-vis spectrum of **5** at solid state upon irradiation with xenon light (at room temperature)

X-ray Structural Analysis of **5**

Single crystals of **5** suitable for X-ray crystallographic analysis were obtained by slow evaporation from the mixture of acetone and ethyl acetate solution at room temperature.

The X-ray diffraction measurements for **5** were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 291 K by using graphite-monochromated Mo K α radiation ($\lambda = 0.71075 \text{ \AA}$). Data were collected by ω scan technique. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined. Please see its CIF files. Relevant data are given in Table S2.

Table S2. Crystallographic details of **5**

Compound	1,1'-azobis(5-methyltetrazole)
Formula	C ₄ H ₆ N ₁₀
Formula weight[g·mol ⁻¹]	194.19
Temperature	291

Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Cell parameters	a=7.0325(17) Å, b=9.9190(12) Å, c=12.4750(6) Å
Cell volume	870.2(2) Å ³
Formula Z	4
Calc. density [g/cm ³]	1.48215
Absorption correction	Multi-scan
Theta range for data collection[°]	3.3-26.0
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I)]	R ₁ =0.0310,wR ₂ =0.0745
R indices (all data)	R ₁ = 0.0320,wR ₂ = 0.0751
Largest diff. peak and hole	0.11 and -0.11 e.Å ⁻³
CCDC	889575

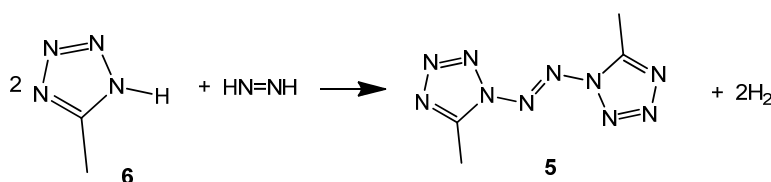
Table S3. Selected bond distances

Parameter	Bond length(Å)	Parameter	Bond length(Å)
N ₁ -N ₂	1.375(2)	N ₇ -N ₈	1.3594(18)
N ₁ -C ₁	1.309(2)	N ₇ -C ₃	1.3501(19)
N ₂ -N ₃	1.285(2)	N ₈ -N ₉	1.290(2)
N ₃ -N ₄	1.3602(19)	N ₉ -N ₁₀	1.373(2)
N ₄ -N ₅	1.3790(17)	N ₁₀ -C ₃	1.309(2)
N ₄ -C ₁	1.3526(19)	C ₁ -C ₂	1.475(2)
N ₅ -N ₆	1.2427(18)	C ₃ -C ₄	1.478(3)
N ₆ -N ₇	1.3805(18)		

Computation details

Computations were carried out by using the Gaussian03 suite of programs. The elementary geometric optimization and the frequency analysis were performed at the level of Becke three Lee-Yan-Parr (B3LYP) Functionals¹ with 6-311+G** basis set². All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies.

The gas phase heat of formation (HOF) of **5** (Table S4) was determined by using the method of permutation reactions³. For the azo compounds reported here, the permutation reactions were carried out as Hakima Abou-Rachid did⁴ (Scheme S1). The accuracy of the method was also proved by the HOF prediction of **5**, as shown in Table S4. According to the optimized structure, the total energy (E_0) and thermodynamic parameters, including zero point energy (ZPE) and thermal correction to Enthalpy (HT), were obtained at the B3LYP/6-311+G** level⁵.



Scheme S1. Permutation reactions for compound **5**

Table S4. The theoretic calculation of heat of formation (HOF) for compound **5**

Compd.	E_0 (a.u)	ZPE ^[a]	H_T (kJ/mol)	HOF (kJ/mol)
5	-703.5359922	342.37	36.57	986.05
H ₂	-1.1795710	25.38	8.68	0.00
5-methyl-1H-tetrazole (6)	-297.6593033	187.22	16.49	280.70 ^[b]
N ₂ H ₂	-110.6795238	70.35	10.03	194.97 ^[c]

[a] Scale factor for ZPE and vibrational frequencies is 0.96.

[b] Kozyro, A. A.; Simirskii, V. V.; Krasulin, A. P. et al. *Russ. J. Phys. Chem. (Engl. Transl.)* **1990**, 64, 348-350.

[c] B. Ruscic; J. Berkowitz. *J. Chem. Phys* **1991**, 95, 4378-4384.

Detonation Parameters

Detonation velocity (D) and detonation pressure (P) were evaluated by the empirical Kamlet formula as

$$P = 1.558 \rho^2 \Phi \quad (1)$$

$$D = 1.01 \Phi^{1/2} (1 + 1.30 p_0) \quad (2)$$

$$\Phi = 0.4889 N (MQ)^{1/2} \quad (3)$$

where D is the predicted detonation velocity (km/s) and P is the detonation pressure (GPa), ρ is the density of a compound (cm³/mol). Φ , N , M and Q are characteristic parameters of an explosive, Q is chemical energy of detonation (kJ/g). The crystal

densities and the calculated heats of formation were used in computing the D and P values.

Reference

- 1 (a) Becke, A. D., *J. Phys. Chem.* **1993**, *98* (7), 5648-5652; (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., *J. Phys. Chem.* **1994**, *98* (45), 11623-11627.
- 2 Hariharan, P. C.; Pople, J. A., *Theoretica Chimica Acta* **1973**, *28* (3), 213-222.
- 3 (a) Schmidt, M. W.; Gordon, M. S.; Boatz, J. A., *J. Phys. Chem. A* **2005**, *109* (32), 7285-7295; (b) Gao, H.; Ye, C.; Piekarski, C. M.; Shreeve, J. M., *J. Phys. Chem. C* **2007**, *111* (28), 10718-10731.
- 4 Jaidann, M.; Roy, S.; Abou-Rachid, H.; Lussier, L. S., *J. Hazard Mater.* **2010**, *176* (1-3), 165-173.
- 5 Pople, J. A.; Binkley, J. S.; Seeger, R., *Int. J. Quantum Chem.* **1976**, *10* (S10), 1-19.