Supporting information

Nitramino-furazan-functionalized fused high-nitrogen backbone as energetic materials with high detonation performance and good molecular stabilities

Wangying Zhu, Zhiwen Ye* and Zhen Dong

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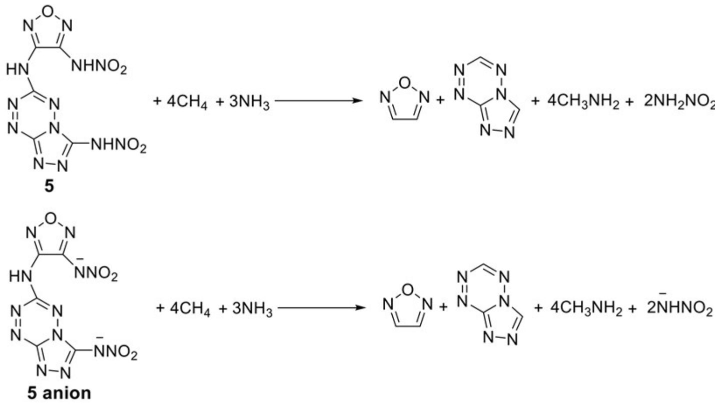
Computational Details

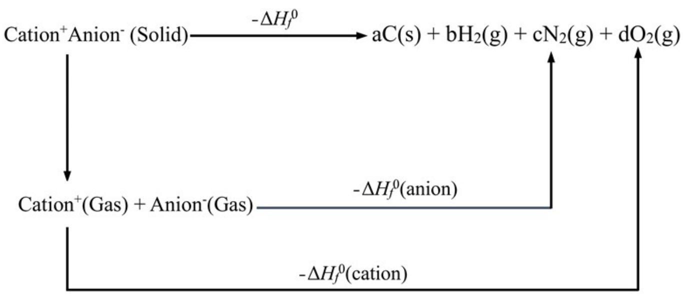
Computations were performed by using the Gaussian09 suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[2] functional with the 6-311++G** basis set.[3] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.[4] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

The predictions of heats of formation (HOF) of compounds used the hybrid DFTB3LYP methods with the 6-311++G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of compounds **5**, and **7-11**are shown in Scheme S1.



Scheme S1 Isodesmic reactions for calculating heats of formation for **5**, and **7-11**.

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (Scheme S2).[5] The number is simplified by equation 1:



Scheme S2 Born-Haber Cycle for the formation of energetic salts.

ΔH_f^o (salt, 298 K) = ΔH_f^o (cation, 298K) + ΔH_f^o (anion, 298K) – ΔH_L (1)
where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [Eq. (2)]
$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (2)
where n_M and n_X depend on the nature of the ions, M^{q+} and X^{p-}, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.
The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:
U_{POT} [kJ mol^{-1}] = $\gamma(\rho_m/M_m)^{1/3} + \delta$ (3)
where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for (g) and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[5]

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. Based on the literature,[6] the heat of sublimation can be estimated with Trouton's rule according to supplementary equation 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{sub} = 188/\text{J mol}^{-1}\text{K}^{-1} \times T$$

Crystallographic data for 4 and 6

Table S1 Crystallographic data of **4** and **6**.

Compd.	**4**	**6**
CCDC number	1912224	1915957
formula	$C_6H_9N_{11}O_2$	$C_5H_{11}N_{13}Na_2O_{10}$
Mw	267.24	459.25
crystal system	Monoclinic	Orthorhombic
space group	$P\,2_1/c$	$P\,2_1\,2_1\,2_1$
color	colorless	colorless
a [Å]	6.9841(4)	6.3798(4)
b [Å]	10.3283(6)	9.9018(7)
c [Å]	15.0301(8)	26.2299(19)
α [°]	90	90
β [°]	94.578(2)	90
γ [°]	90	90
V [Å^3]	1080.72(11)	1657.0(2)
Z	4	4
T [K]	253(2)	193(2)
λ [Å]	1.34139	1.34139
ρ_{calcd} [g cm^{-3}]	1.642	1.841
μ [mm^{-1}]	0.719	1.236
F (000)	552	936
θ range [°]	5.137-53.940	2.931-54.138
Data/restraints/parameter	1911/0/174	3022/0/271
S	0.993	1.008
R_1 [$I > 2\sigma(I)$]	0.0432(1787)	0.0490(2450)
wR_2 [$I > 2\sigma(I)$]	0.1099(1911)	0.1219(3022)

Table S2 Selected bond lengths [Å] and angles [°] for compound **4**.

C1-N1	1.303(2)	N6-C3-N5	128.42(16)
C1-N3	1.345(2)	N4-C3-N5	111.10(14)
C1-C2	1.443(2)	N9-C4-N8	128.73(17)
C2-N2	1.298(2)	N9-C4-N7	109.87(16)
C2-N4	1.369(2)	N8-C4-N7	121.37(16)
C3-N6	1.303(2)	N11-C5-N10	127.18(17)
C3-N4	1.366(2)	N11-C5-N7	124.62(17)
C3-N5	1.404(2)	N10-C5-N7	108.19(16)
C4-N9	1.320(2)	O2-C6-H6A	109.5
C4-N8	1.339(2)	O2-C6-H6B	109.5
C4-N7	1.381(2)	H6A-C6-H6B	109.5
C5-N11	1.327(2)	O2-C6-H6C	109.5
C5-N10	1.346(2)	H6A-C6-H6C	109.5
C5-N7	1.348(2)	H6B-C6-H6C	109.5
C6-O2	1.411(3)	C1-N1-O1	106.08(14)
C6-H6A	0.9700	C2-N2-O1	105.72(14)
C6-H6B	0.9700	C1-N3-H3A	120.0
C6-H6C	0.9700	C1-N3-H3B	120.0
N1-O1	1.392(2)	H3A-N3-H3B	120.0
N2-O1	1.391(2)	C3-N4-C2	125.73(15)
N3-H3A	0.8700	C3-N4-H4	117.1
N3-H3B	0.8700	C2-N4-H4	117.1
N4-H4	0.8700	N8-N5-C3	118.99(15)
N5-N8	1.296(2)	C3-N6-N7	109.99(14)
N6-N7	1.372(2)	C5-N7-N6	129.82(15)
N9-N10	1.366(2)	C5-N7-C4	106.25(15)
N11-H11A	0.8700	N6-N7-C4	123.93(14)
N11-H11B	0.8700	N5-N8-C4	117.25(15)
O2-H2	0.8300	C4-N9-N10	106.70(15)
N1-C1-N3	124.33(16)	C5-N10-N9	108.99(15)
N1-C1-C2	108.43(16)	C5-N11-H11A	120.0
N3-C1-C2	127.22(16)	C5-N11-H11B	120.0
N2-C2-N4	125.67(16)	H11A-N11-H11B	120.0
N2-C2-C1	109.37(16)	N1-O1-N2	110.40(12)
N4-C2-C1	124.94(16)	C6-O2-H2	109.5
N6-C3-N4	120.47(16)		

Table S3 Hydrogen bonds present in compound **4**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
O2-H···N2	0.83	2.06	2.868(2)	163.00
O2-H···N6	0.83	2.57	3.119(2)	125.00
N3-H3A···N5	0.87	2.24	3.060(2)	158.00
N3-H3B···O1	0.87	2.17	2.995(2)	158.00
N3-H3B···N1	0.87	2.44	3.290(2)	166.00
N4-H4···N1	0.87	2.13	2.996(2)	176.00

N11-H11A···N9	0.87	2.24	3.007(2)	147.00
N11-H11B···O2	0.87	1.98	2.827(2)	166.00

Table S4 Selected bond lengths [Å] and angles [°] for compound **6**.

C1-N3	1.312(7)	N3-C1-N2	133.5(5)
C1-N2	1.365(6)	N3-C1-C2	108.3(4)
C1-C2	1.437(6)	N2-C1-C2	118.1(5)
C2-N4	1.305(6)	N4-C2-N5	126.8(4)
C2-N5	1.370(7)	N4-C2-C1	110.6(5)
C3-N6	1.306(6)	N5-C2-C1	122.7(4)
C3-N5	1.361(6)	N6-C3-N5	121.8(5)
C3-N7	1.413(7)	N6-C3-N7	127.4(5)
C4-N10	1.314(6)	N5-C3-N7	110.7(4)
C4-N8	1.354(6)	N10-C4-N8	128.2(5)
C4-N9	1.370(7)	N10-C4-N9	110.6(4)
C5-N11	1.345(7)	N8-C4-N9	121.1(5)
C5-N12	1.357(7)	N11-C5-N12	131.9(4)
C5-N9	1.361(5)	N11-C5-N9	108.3(5)
N1-O1	1.241(5)	N12-C5-N9	119.2(5)
N1-O2	1.267(5)	O1-N1-O2	121.2(4)
N1-N2	1.321(6)	O1-N1-N2	123.7(4)
N1-Na2	3.037(5)	O2-N1-N2	115.1(4)
N2-Na2	2.799(5)	O1-N1-Na2	164.6(3)
N3-O3	1.396(5)	O2-N1-Na2	49.4(2)
N4-O3	1.403(6)	N2-N1-Na2	67.0(3)
N5-H5	1.0086	N1-N2-C1	117.6(4)
N6-N9	1.361(6)	N1-N2-Na2	87.3(3)
N7-N8	1.283(6)	C1-N2-Na2	152.1(3)
N10-N11	1.361(6)	C1-N3-O3	105.6(4)
N11-Na1	2.428(5)	C2-N4-O3	104.4(4)
N12-N13	1.307(5)	C3-N5-C2	125.9(4)
N13-O4	1.243(6)	C3-N5-H5	111.9
N13-O5	1.287(6)	C2-N5-H5	122.1
Na1-O4W	2.296(4)	C3-N6-N9	110.3(4)
Na1-O2	2.322(4)	N8-N7-C3	119.6(4)
Na1-O5	2.396(4)	N7-N8-C4	116.8(5)
Na1-O3W	2.455(5)	N6-N9-C5	129.9(4)
Na1-O4	2.544(5)	N6-N9-C4	124.6(4)
Na1-Na2	3.625(3)	C5-N9-C4	105.5(4)
Na1-Na2	3.821(3)	C4-N10-N11	106.9(4)
Na1-H4WA	2.5558	C5-N11-N10	108.7(4)
Na2-O4W	2.391(5)	C5-N11-Na1	126.3(3)
Na2-O2	2.413(5)	N10-N11-Na1	111.7(3)
O4-Na1-Na2	44.19(9)	N13-N12-C5	116.4(4)
Na2-Na1-Na2	118.30(5)	O4-N13-O5	120.0(4)
O4W-Na1-H4WA	17.6	O4-N13-N12	125.1(4)
O2-Na1-H4WA	76.6	O5-N13-N12	115.0(4)
O5-Na1-H4WA	168.9	O4W-Na1-O2	94.14(13)
N11-Na1-H4WA	102.7	O4W-Na1-O5	159.09(16)
O3W-Na1-H4WA	79.4	O2-Na1-O5	102.54(13)
O4-Na1-H4WA	94.1	O4W-Na1-N11	88.75(14)
Na2-Na1-H4WA	45.7	O2-Na1-N11	147.03(19)
Na2-Na1-H4WA	78.8	O5-Na1-N11	84.10(13)
O4W-Na2-O2	159.75(15)	O4W-Na1-O3W	81.29(14)
O4W-Na2-O5W	82.02(14)	O2-Na1-O3W	78.97(14)
O2-Na2-O5W	101.12(14)	O5-Na1-O3W	89.54(14)
O4W-Na2-O3W	78.81(14)	N11-Na1-O3W	133.79(17)
O2-Na2-O3W	93.59(14)	O4W-Na1-O4	98.31(15)
O5W-Na2-O3W	158.37(16)	O2-Na1-O4	80.80(15)
O4W-Na2-O1W	111.13(15)	O5-Na1-O4	96.74(15)
O2-Na2-O1W	84.93(14)	N11-Na1-O4	66.30(14)
Na2-O1W-H1WB	118	O3W-Na1-O4	159.68(14)
H1WA-O1W-H1WB	96.1	O4W-Na1-Na2	40.31(11)
H2WA-O2W-H2WB	95.9	O2-Na1-Na2	96.00(12)
Na1-O3W-Na2	94.35(15)	O5-Na1-Na2	124.05(13)
Na1-O3W-H3WA	104.3	N11-Na1-Na2	106.97(12)
Na2-O3W-H3WA	121.2	O3W-Na1-Na2	43.16(9)
Na1-O3W-H3WB	152.6	O4-Na1-Na2	138.47(11)
Na2-O3W-H3WB	81.6	O4W-Na1-Na2	93.46(11)
H3WA-O3W-H3WB	100.8	O2-Na1-Na2	37.03(11)
Na1-O4W-Na2	101.28(16)	O5-Na1-Na2	107.45(11)
Na1-O4W-H4WA	100.4	N11-Na1-Na2	110.05(14)
Na2-O4W-H4WA	96.2	O3W-Na1-Na2	115.49(10)
Na1-O4W-H4WB	126.6	Na2-O5W-H5WB	103.9
Na2-O4W-H4WB	112.7	H5WA-O5W-H5WB	113.1
H4WA-O4W-H4WB	114.8	Na2-O5W-H5WA	127.4

Table S5 Hydrogen bonds present in compound **6**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
O1W-H1WA···N12	1.03	1.90	2.931(6)	172.00
O1W-H1WB···N4	0.91	2.06	2.957(5)	168.00
O2W-H2WA···N7	0.82	2.13	2.937(6)	171.00
O2W-H2WA···N8	0.82	2.46	3.196(5)	150.00
O2W-H2WB···O1	0.80	2.38	2.856(5)	119.00
O2W-H2WB···N3	0.80	2.15	2.923(6)	163.00

N5-H5···O5W	1.01	1.82	2.818(5)	171.00
O3W-H3WA···O1	0.88	2.13	2.967(5)	157.00
O3W-H3WB…O5	0.84	2.19	2.986(6)	157.00
O4W-H4WA…O5	0.78	2.05	2.821(5)	168.00
O4W-H4WB…O2W	0.96	1.74	2.665(5)	160.00
05W-H5WA…N10	0.83	2.07	2.870(6)	162.00
O5-H5WB…O1W	0.94	1.93	2.842(5)	161.00

IR and NMR spectra

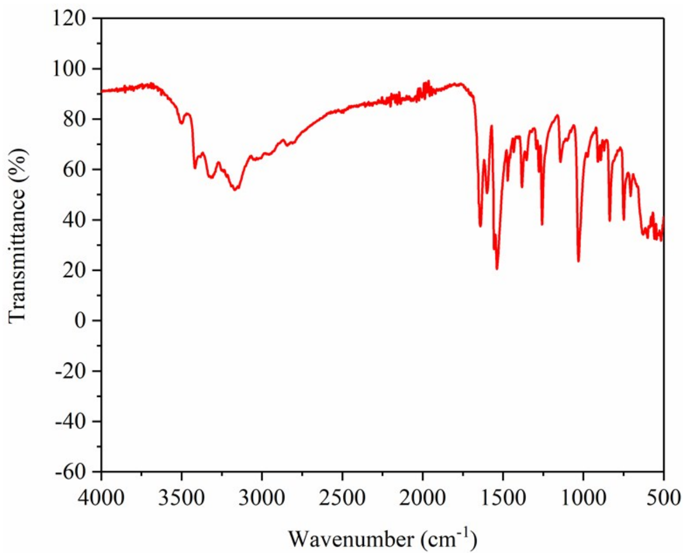


Fig. S1 IR spectra for **4**.

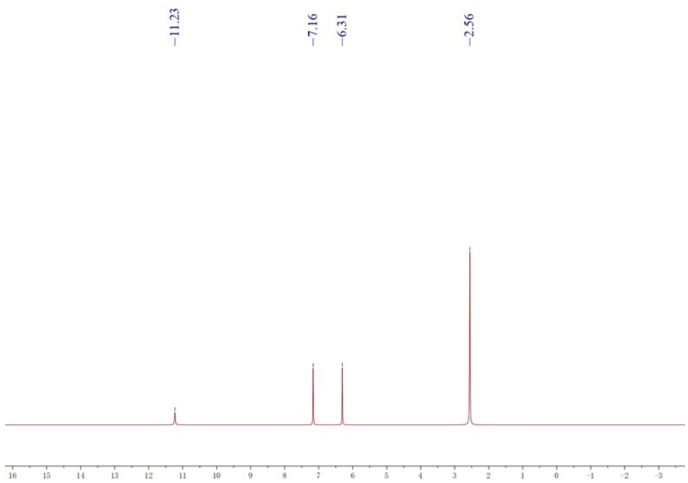


Fig. S2 ^{1}H NMR spectra in DMSO-d_6 for **4**.

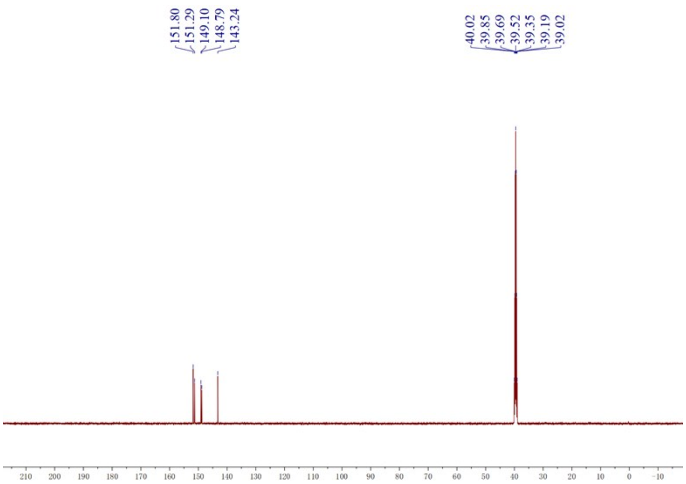


Fig. S3 ^{13}C NMR spectra in DMSO-d_6 for **4**.

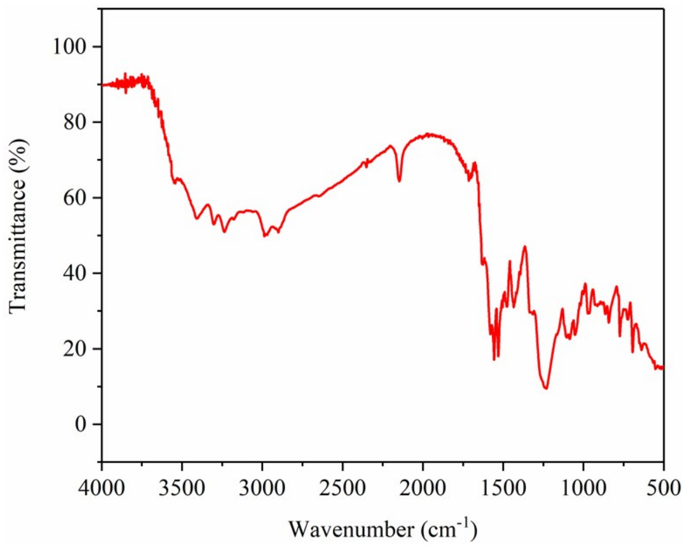


Fig. S4 IR spectra for **5**.

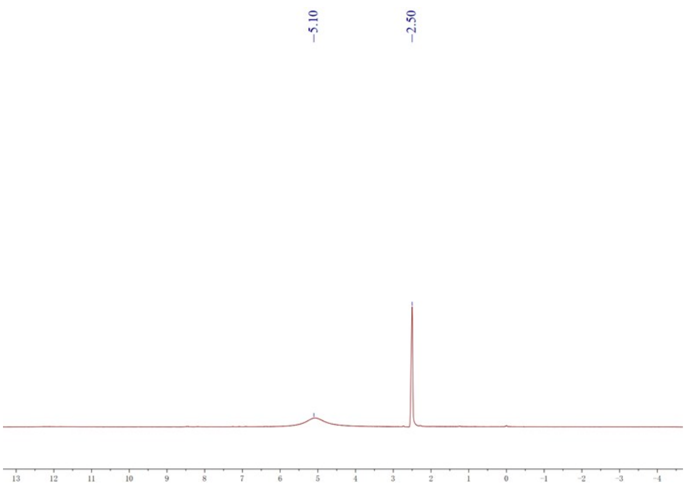


Fig. S5 ^{1}H NMR spectra in DMSO-d_6 for **5**.

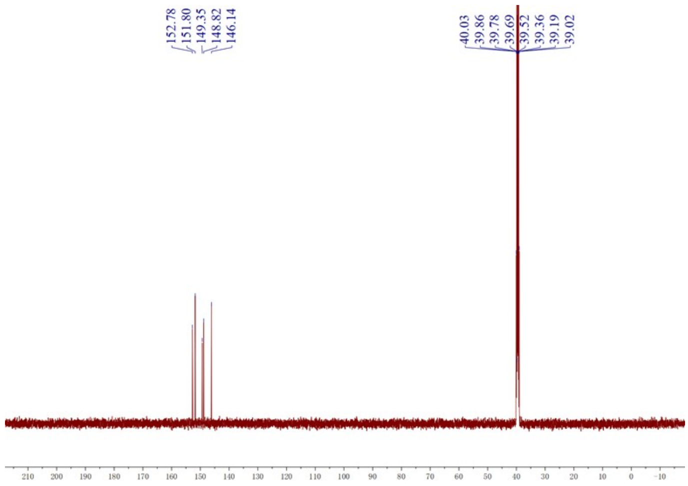


Fig. S6 ^{13}C NMR spectra in DMSO-d_6 for **5**.

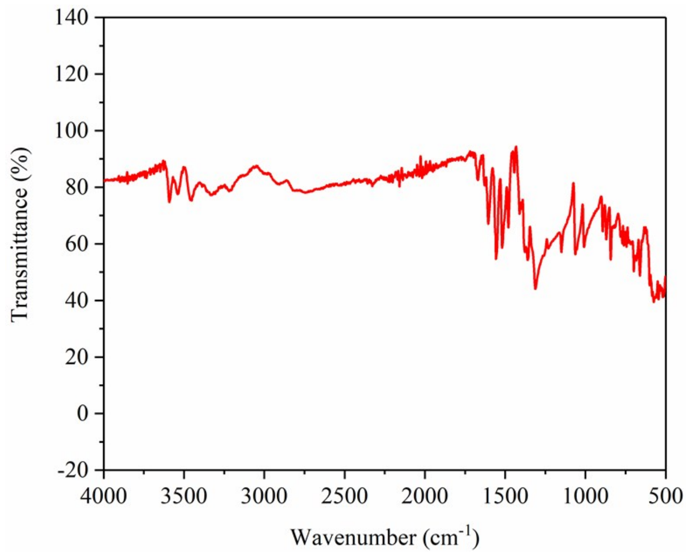


Fig. S7 IR spectra for **6**.

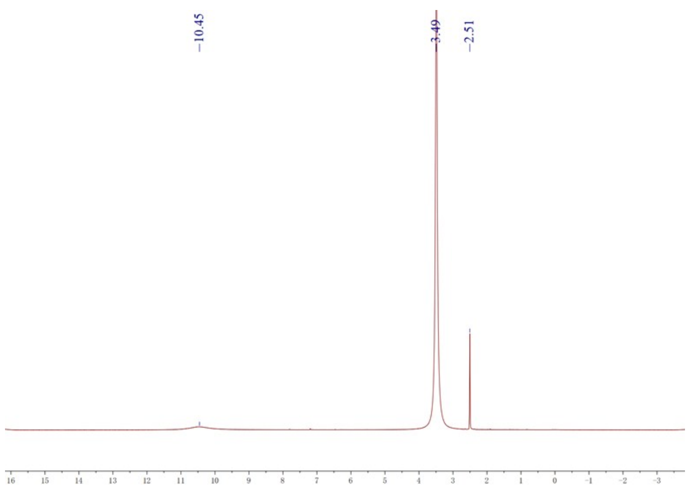


Fig. S8 ^{1}H NMR spectra in DMSO-d_6 for **6**.

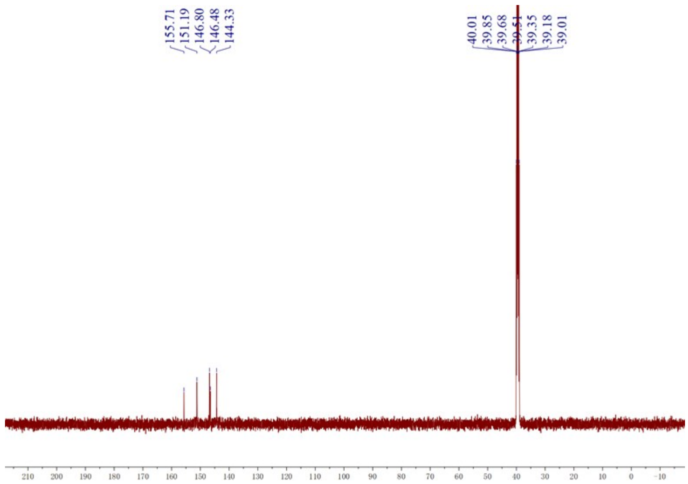


Fig. S9 ^{13}C NMR spectra in DMSO-d_6 for **6**.

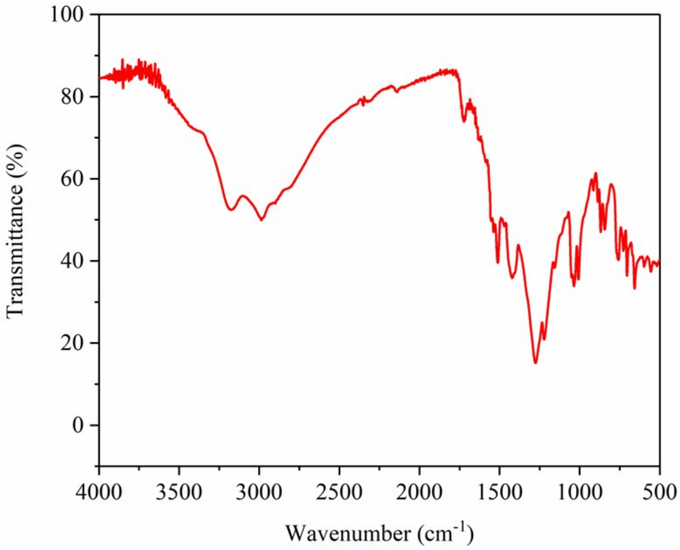


Fig. S10 IR spectra for **7**.

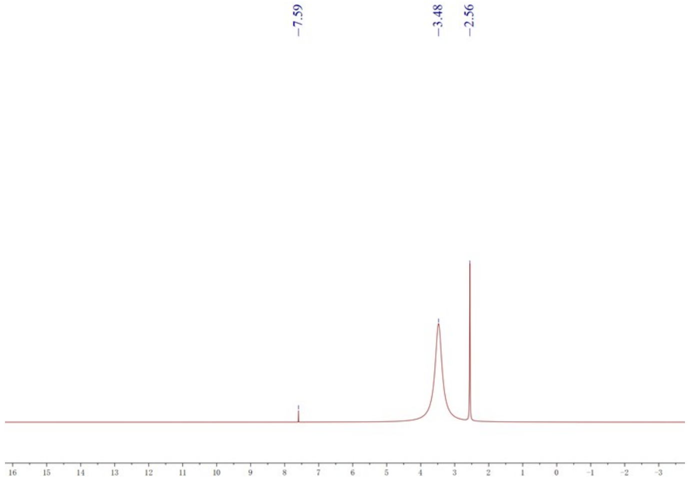


Fig. S11 ^{1}H NMR spectra in DMSO-d_6 for **7**.

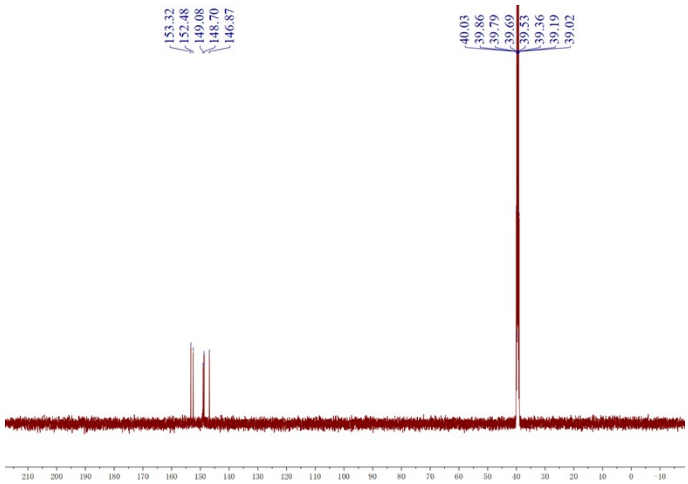


Fig. S12 ^{13}C NMR spectra in DMSO-d_6 for **7**.

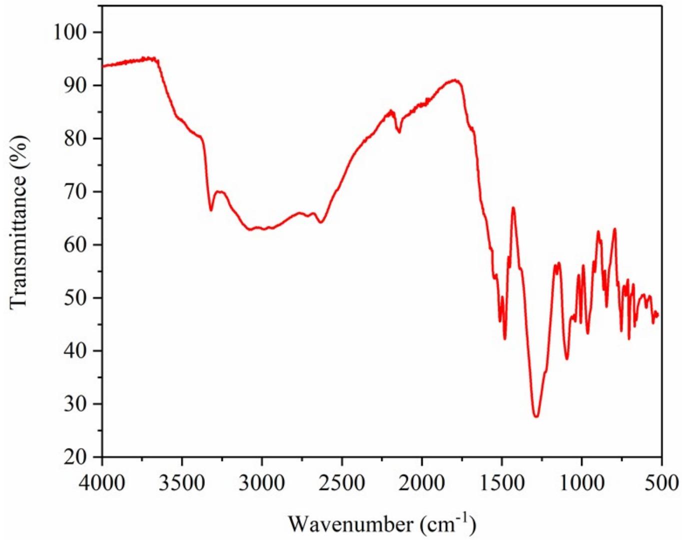


Fig. S13 IR spectra for **8**.

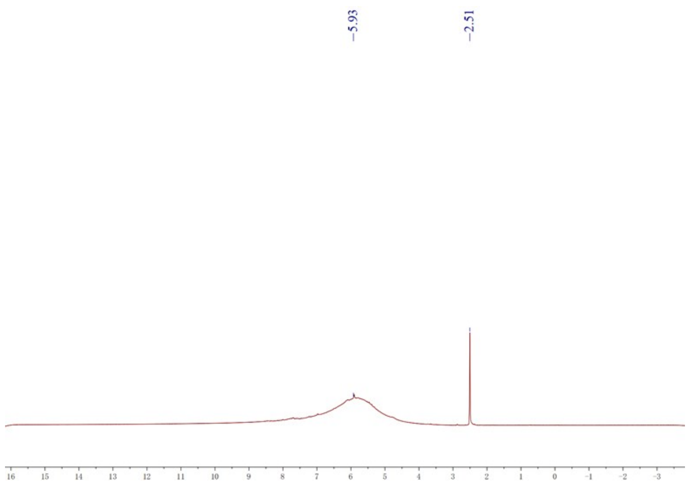


Fig. S14 ^{1}H NMR spectra in DMSO-d_6 for **8**.

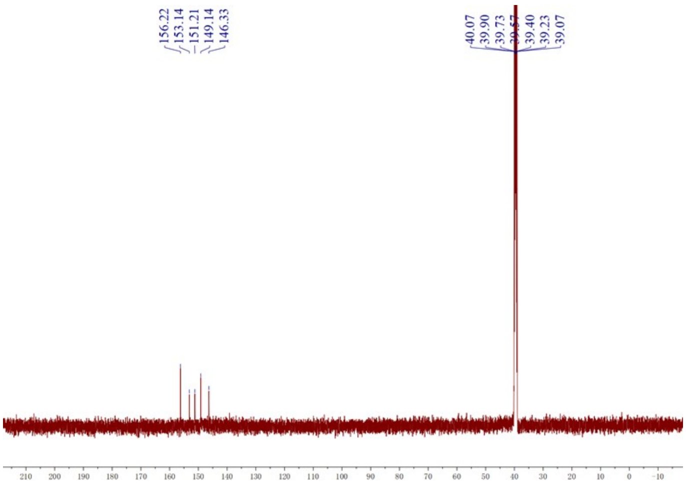


Fig. S15 ^{13}C NMR spectra in DMSO-d_6 for **8**.

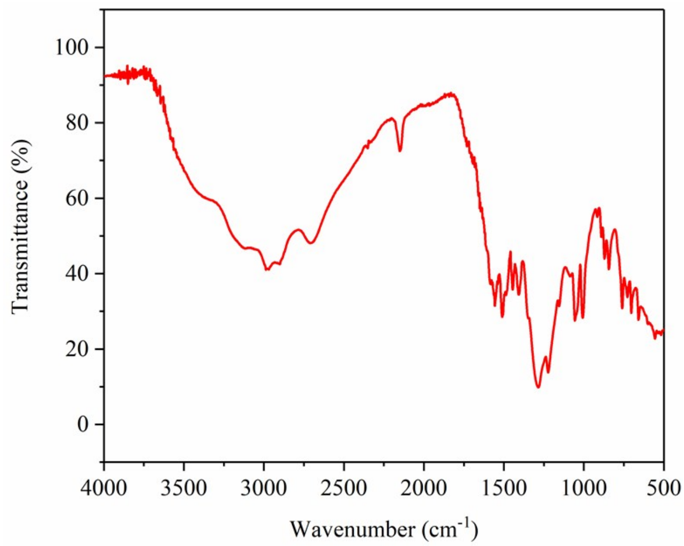


Fig. S16 IR spectra for **9**.

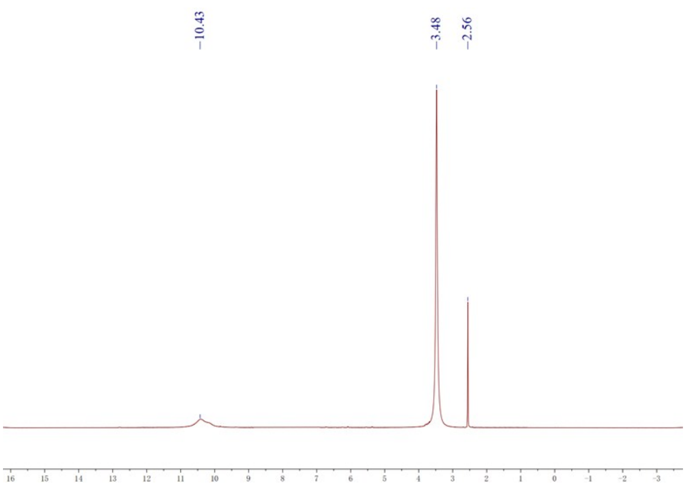


Fig. S17 ^{1}H NMR spectra in DMSO-d_6 for **9**.

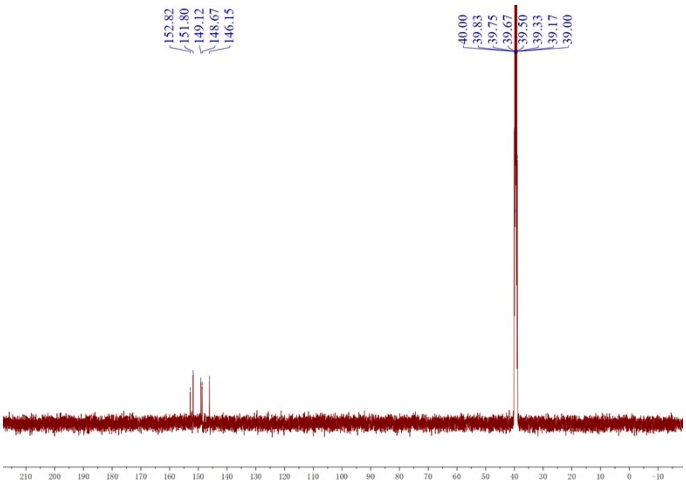


Fig. S18 ^{13}C NMR spectra in DMSO-d_6 for **9**.

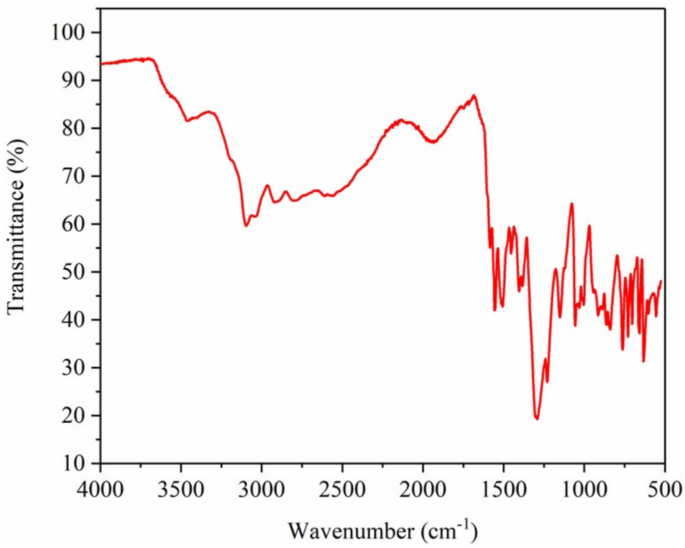


Fig. S19 IR spectra for **10**.

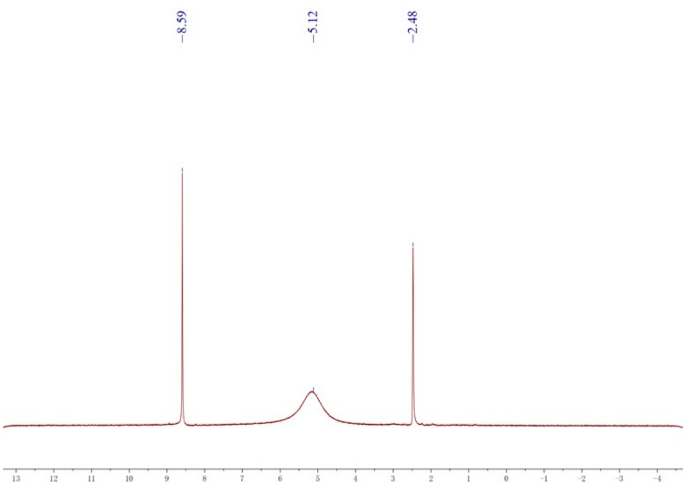


Fig. S20 ^{1}H NMR spectra in DMSO-d_6 for **10**.

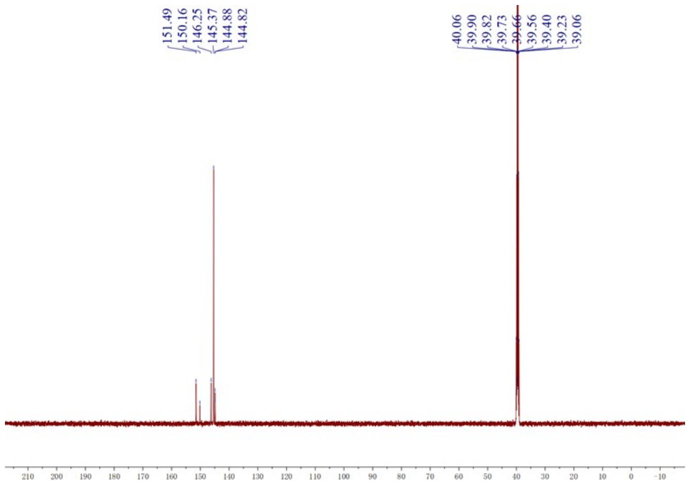


Fig. S21 ^{13}C NMR spectra in DMSO-d_6 for **10**.

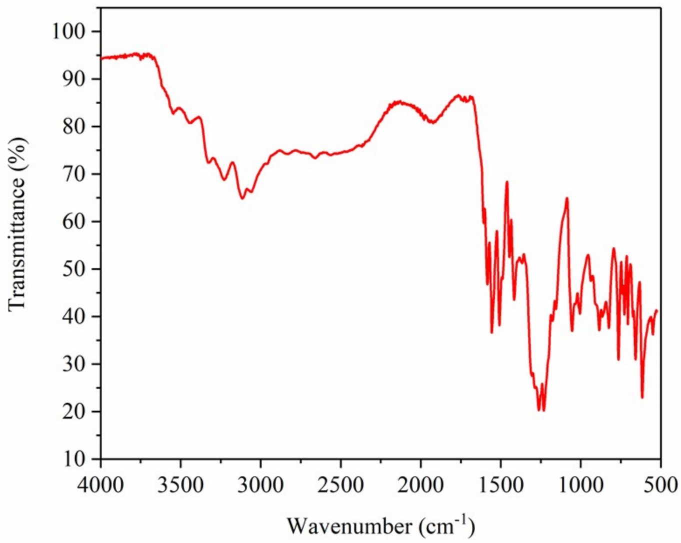


Fig. S22 IR spectra for **11**.

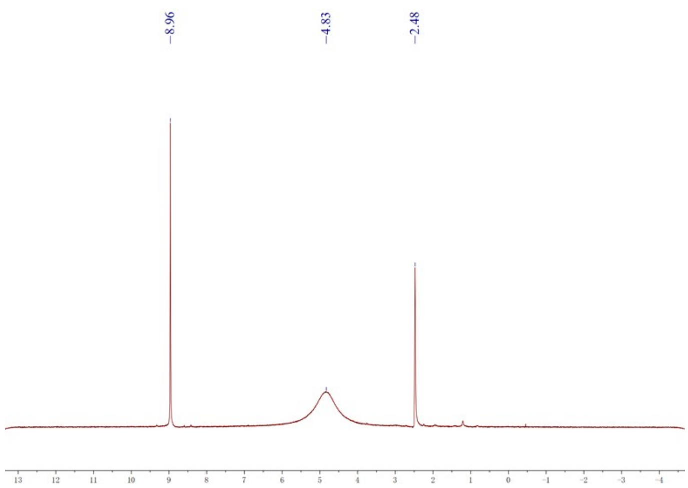


Fig. S23 ^{1}H NMR spectra in DMSO-d_6 for **11**.

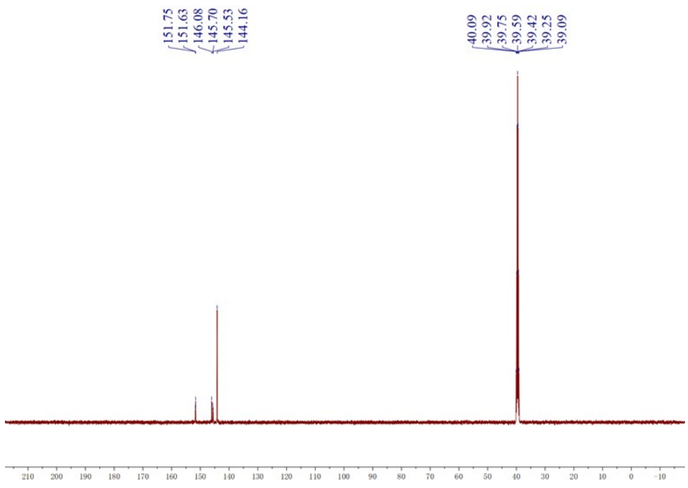


Fig. S24 ^{13}C NMR spectra in DMSO-d_6 for **11**.

DSC curves

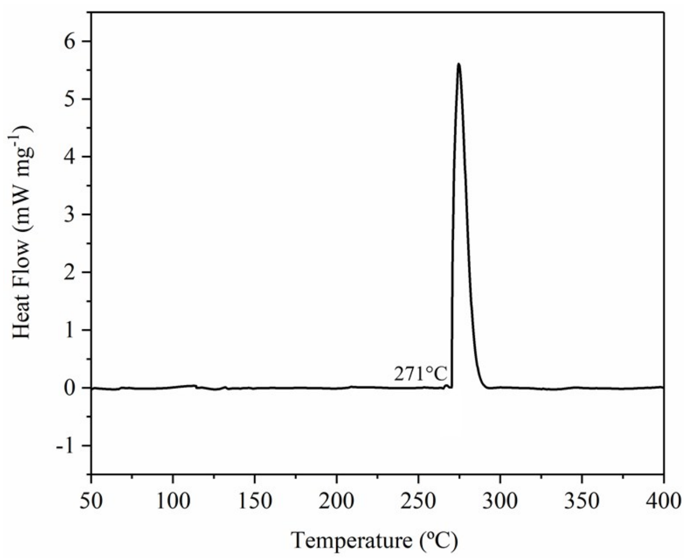


Fig. S25 DSC plot of **4** easured at a heating rate of 5 °C min^{-1} (exo up).

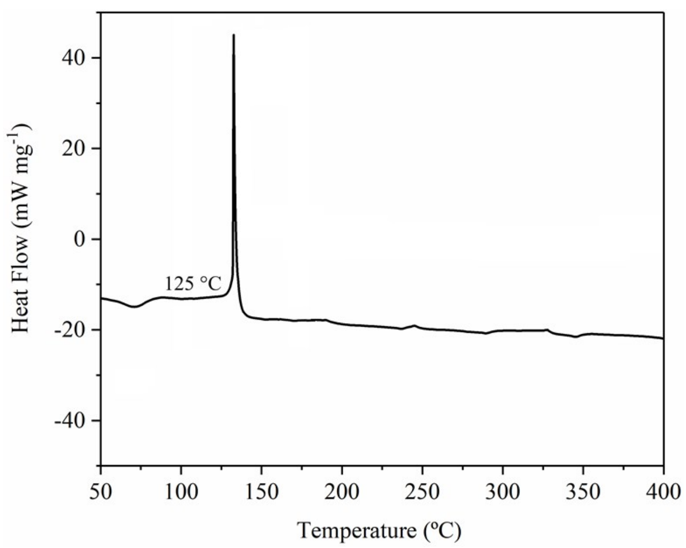


Fig. S26 DSC plot of **5** measured at a heating rate of 5 °C min^{-1} (exo up).

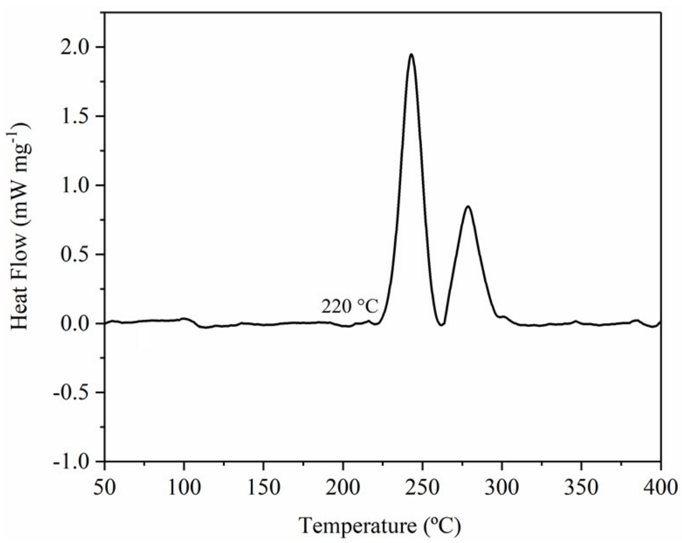


Fig. S27 DSC curve of **6** measured at a heating rate of 5 °C min^{-1} (exo up).

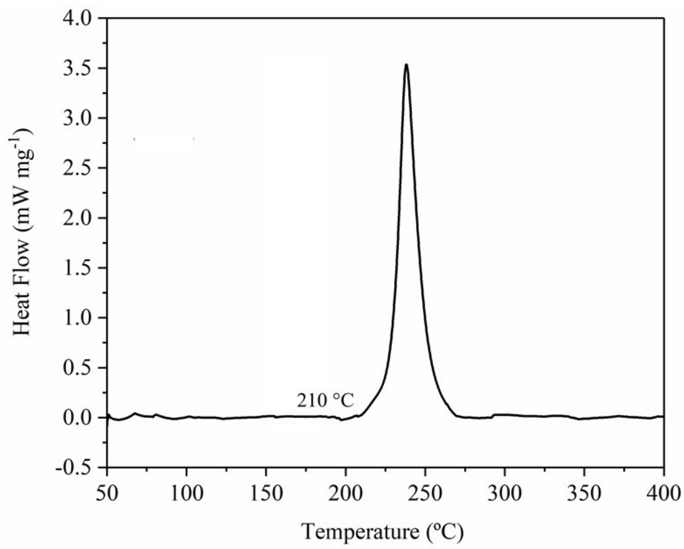


Fig. S28 DSC curve of **7** measured at a heating rate of 5 °C min^{-1} (exo up).

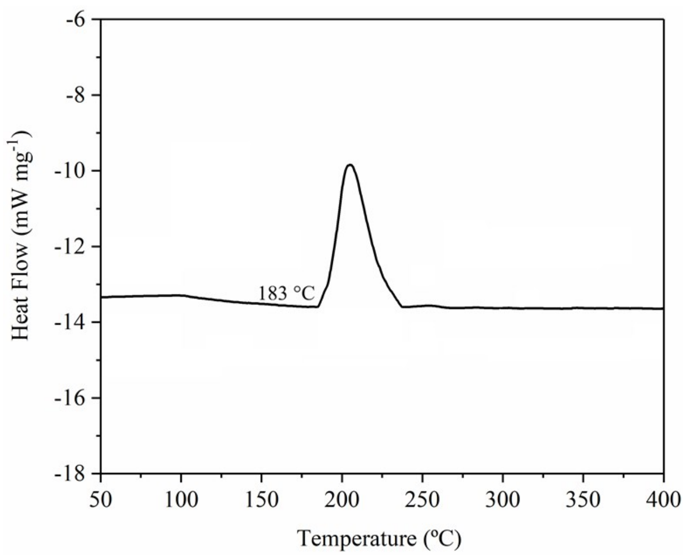


Fig. S29 DSC curve of **8** measured at a heating rate of 5 °C min^{-1} (exo up).

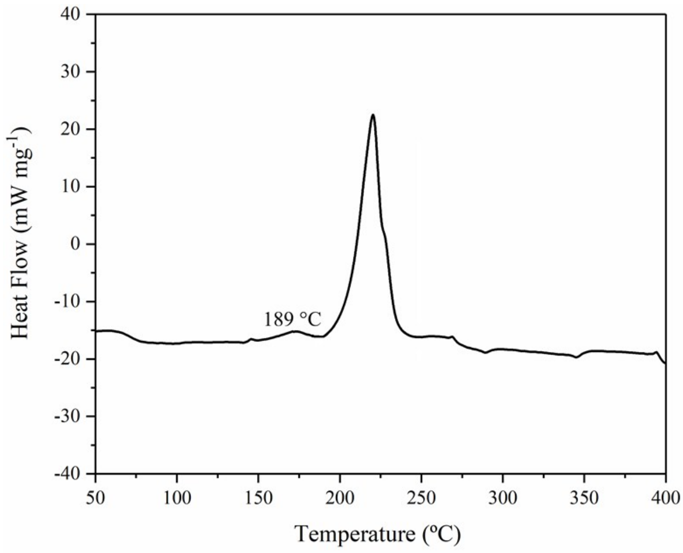


Fig. S30 DSC curve of **9** measured at a heating rate of 5 °C min^{-1} (exo up).

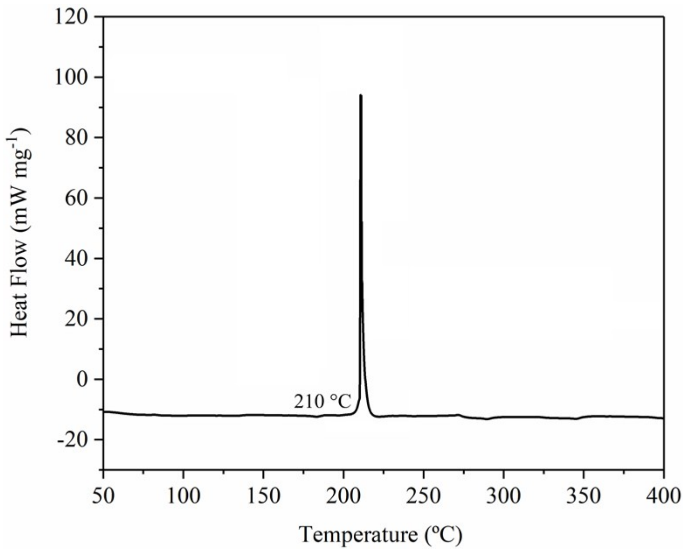


Fig. S31 DSC curve of **10** measured at a heating rate of 5 °C min^{-1} (exo up).

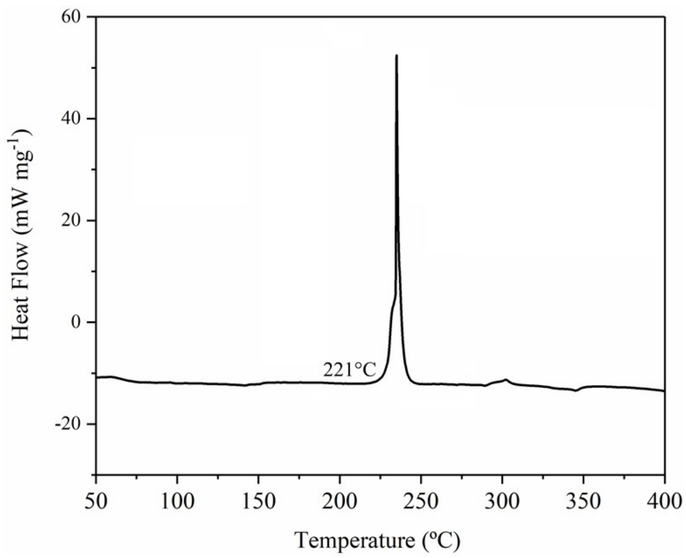


Fig. S32s DSC curve of **11** measured at a heating rate of 5 °C min^{-1} (exo up).

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