Electronic Supplementary Information

Improving the Density and Properties of Nitrogen-rich Scaffolds by Introduction of a C-NO_2 group

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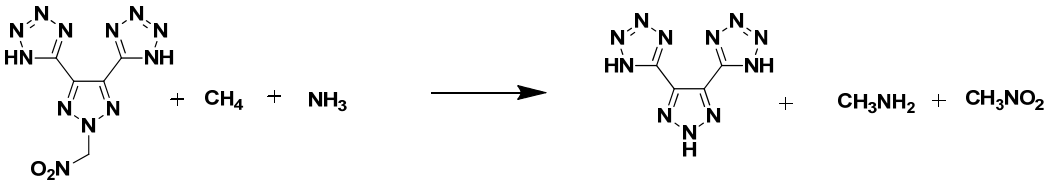


Crystallographic Data

Table S1. Crystal data and structure refinement for Pd complex of **2** and sodium salt of **3**

Empirical formula	**$C_{14}H_{32}N_{18}O_4PdS_4$**	**$C_3H_4N_9NaO_3$**
CCDC	1578028	1578029
Formula weight	751.21	237.14
Temperature	150(2) K	150(2) K
Wavelength	1.54178 Å	P21/c
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pbcm
a /Å	8.0774(6)	8.3610(11)
b /Å	9.3329(7)	15.124(2)
c /Å	10.9899(8)	6.2921(8)
α (°)	96.638(3)	90°
β (°)	108.728(3)	90°
γ (°)	107.974(4)	90°
V /Å3	724.82(10)	795.62(18)
Z	1	4
ρ calc g/cm3 (-123°C)	1.721	1.980
ρ calc g/cm3 (20°C)	1.688	1.952
Absorption coefficient/ mm-1	8.373	0.215
F(000)	384	480
Crystal size/mm3	0.084 x 0.076 x 0.035	0.259 x 0.049 x 0.040
Theta range for data collection	4.374 to 75.115°.	2.784 to 30.000°.
Index ranges	-9<=h<=9, -11<=k<=8, -12<=l<=12	-11<=h<=10, -19<=k<=20, -8<=l<=8
Reflections collected	4883	8493
Independent reflections	2359 [Rint = 0.0356]	1239 [R_{int} = 0.0424]
Completeness to theta°	67.679°/ 83.5 %	25.242°/ 99.7 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.5208	0.7460 and 0.6878
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2359 / 0 / 193	1239 / 3 / 100
Goodness-of-fit on F2	1.084	1.064
Final R indices [I>2sigma(I)]	R_1 = 0.0557, wR_2 = 0.0913	R_1 = 0.0346, wR_2 = 0.0828
R indices (all data)	R_1 = 0.0346, wR_2 = 0.0828	R_1 = 0.0557, wR_2 = 0.0913
Largest diff. peak and hole/ e.Å^{-3}	0.398 and -0.267	0.398 and -0.267 e.Å^{-3}

Table S2. Bond lengths [Å] and angles [°] for Pd complex of 2

N(1)-C(5)	1.324(8)	N(1)-N(2)	1.365(7)
N(1)-Pd(13)	2.010(5)	N(2)-N(3)	1.297(7)
N(3)-N(4)	1.372(7)	N(4)-C(5)	1.318(8)
C(5)-C(6)	1.514(8)	C(6)-N(7)	1.466(7)
C(6)-C(8)	1.505(8)	C(6)-H(6)	1.0000

N(7)-H(7A)	0.9100	N(7)-H(7B)	0.9100
N(7)-H(7C)	0.9100	C(8)-N(9)	1.317(8)
C(8)-N(12)	1.346(8)	N(9)-N(10)	1.365(7)
N(10)-N(11)	1.316(7)	N(11)-N(12)	1.355(7)
N(12)-Pd(13)	1.996(5)	Pd(13)-N(12)#1	1.996(5)
Pd(13)-N(1)#1	2.010(5)	C(14)-S(15)	1.788(7)
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	S(15)-O(16)	1.523(5)
S(15)-C(17)	1.766(6)	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-S(19)	1.775(8)	C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800	C(18)-H(18C)	0.9800
S(19)-O(20)	1.516(4)	S(19)-C(21)	1.767(7)
C(21)-H(21A)	0.9800	C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800		
C(5)-N(1)-N(2)	105.9(5)	C(5)-N(1)-Pd(13)	127.9(4)
N(2)-N(1)-Pd(13)	125.7(4)	N(3)-N(2)-N(1)	107.6(5)
N(2)-N(3)-N(4)	110.5(5)	C(5)-N(4)-N(3)	104.1(5)
N(4)-C(5)-N(1)	111.9(5)	N(4)-C(5)-C(6)	125.3(5)
N(1)-C(5)-C(6)	122.8(5)	N(7)-C(6)-C(8)	109.4(5)
N(7)-C(6)-C(5)	110.3(5)	C(8)-C(6)-C(5)	109.7(5)
N(7)-C(6)-H(6)	109.1	C(8)-C(6)-H(6)	109.1
C(5)-C(6)-H(6)	109.1	C(6)-N(7)-H(7A)	109.5
C(6)-N(7)-H(7B)	109.5	H(7A)-N(7)-H(7B)	109.5
C(6)-N(7)-H(7C)	109.5	H(7A)-N(7)-H(7C)	109.5
H(7B)-N(7)-H(7C)	109.5	N(9)-C(8)-N(12)	111.4(5)
N(9)-C(8)-C(6)	126.4(5)	N(12)-C(8)-C(6)	122.2(5)
C(8)-N(9)-N(10)	104.6(5)	N(11)-N(10)-N(9)	110.5(5)
N(10)-N(11)-N(12)	107.5(5)	C(8)-N(12)-N(11)	106.0(5)
C(8)-N(12)-Pd(13)	128.2(4)	N(11)-N(12)-Pd(13)	125.6(4)
N(12)-Pd(13)-N(12)#1	180.0	N(12)-Pd(13)-N(1)	85.89(19)
N(12)#1-Pd(13)-N(1)	94.11(19)	N(12)-Pd(13)-N(1)#1	94.11(19)
N(12)#1-Pd(13)-N(1)#1	85.89(19)	N(1)-Pd(13)-N(1)#1	180.0
S(15)-C(14)-H(14A)	109.5	S(15)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	S(15)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
O(16)-S(15)-C(17)	105.1(3)	O(16)-S(15)-C(14)	105.4(3)
C(17)-S(15)-C(14)	98.2(3)	S(15)-C(17)-H(17A)	109.5
S(15)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
S(15)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	S(19)-C(18)-H(18A)	109.5
S(19)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
S(19)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	O(20)-S(19)-C(21)	106.1(3)
O(20)-S(19)-C(18)	106.1(3)	C(21)-S(19)-C(18)	97.7(4)
S(19)-C(21)-H(21A)	109.5	S(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5	S(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5	H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Table S3. Hydrogen bonds for Pd complex of 2 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(7)-H(7A)...O(20)#2	0.91	2.13	2.985(7)	155.9
N(7)-H(7B)...O(16)	0.91	1.85	2.738(7)	166.2
N(7)-H(7C)...O(20)	0.91	1.85	2.758(7)	173.1

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z #2 -x+2,-y+1,-z+1

Table S4. Bond lengths [Å] and angles [°] for sodium salt of 3.

N(1)-N(2)	1.341(2)	N(1)-C(5)	1.353(2)
N(1)-H(1)	0.8800	N(2)-N(3)	1.290(2)
N(3)-N(4)	1.364(2)	N(4)-C(5)	1.339(2)
C(5)-C(6)	1.441(3)	C(6)-N(7)	1.360(2)
C(6)-C(10)	1.448(3)	N(7)-O(8)	1.269(2)

N(7)-O(9)	1.272(2)	C(10)-N(11)	1.338(2)
C(10)-N(14)	1.346(2)	N(11)-N(12)	1.372(2)
N(12)-N(13)	1.290(2)	N(13)-N(14)	1.343(2)
N(14)-H(14)	0.8800	O(16)-Na(15)#7	2.3247(12)
O(16)-H(16B)	0.833(9)	O(16)-H(16A)	0.836(10)
N(2)-N(1)-C(5)	109.08(15)	N(2)-N(1)-H(1)	125.5
C(5)-N(1)-H(1)	125.5	N(3)-N(2)-N(1)	106.68(15)
N(2)-N(3)-N(4)	111.21(15)	C(5)-N(4)-N(3)	105.70(15)
N(4)-C(5)-N(1)	107.33(16)	N(4)-C(5)-C(6)	125.95(16)
N(1)-C(5)-C(6)	126.72(17)	N(7)-C(6)-C(5)	118.19(16)
N(7)-C(6)-C(10)	119.27(16)	C(5)-C(6)-C(10)	122.53(16)
O(8)-N(7)-O(9)	119.40(15)	O(8)-N(7)-C(6)	120.03(16)
O(9)-N(7)-C(6)	120.57(15)	N(11)-C(10)-N(14)	107.72(16)
N(11)-C(10)-C(6)	126.38(17)	N(14)-C(10)-C(6)	125.90(17)
C(10)-N(11)-N(12)	105.36(15)	N(13)-N(12)-N(11)	111.08(15)
N(12)-N(13)-N(14)	106.61(15)	N(13)-N(14)-C(10)	109.23(15)
N(13)-N(14)-H(14)	125.4	C(10)-N(14)-H(14)	125.4
H(16B)-O(16)-H(16A)	117(2)		

Table S5. Hydrogen bonds for sodium salt of 3 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(8)	0.88	1.99	2.524(2)	118.1
N(1)-H(1)...N(12)#1	0.88	2.24	3.026(2)	148.2
N(14)-H(14)...N(3)#2	0.88	2.11	2.934(2)	156.5
N(14)-H(14)...O(9)	0.88	2.01	2.560(2)	119.1
O(16)-H(16B)...N(2)#3	0.833(9)	2.029(10)	2.862(2)	179(2)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 -x+1,y-1/2,-z+3/2 #3 x-1,-y+3/2,z-1/2

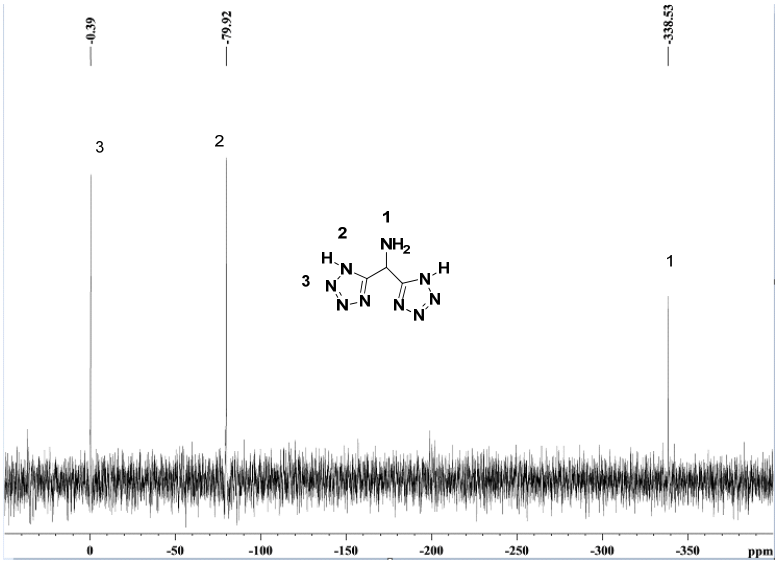
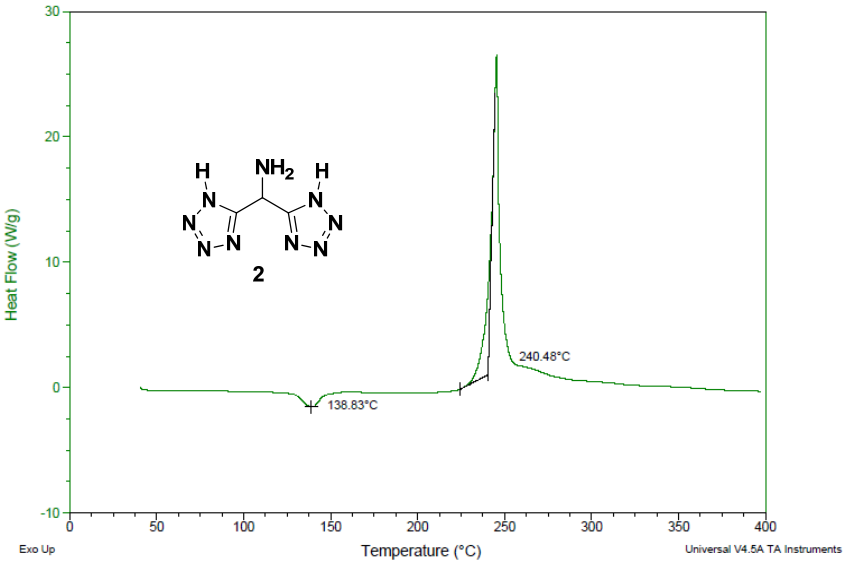
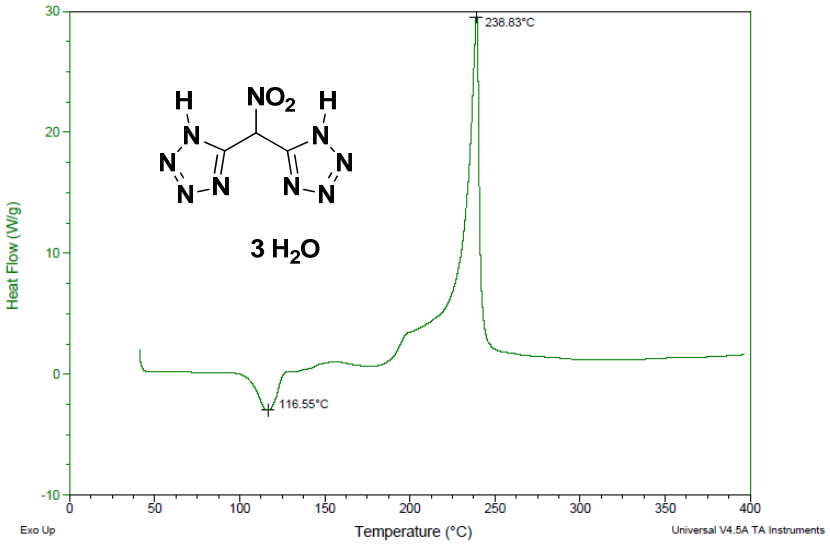
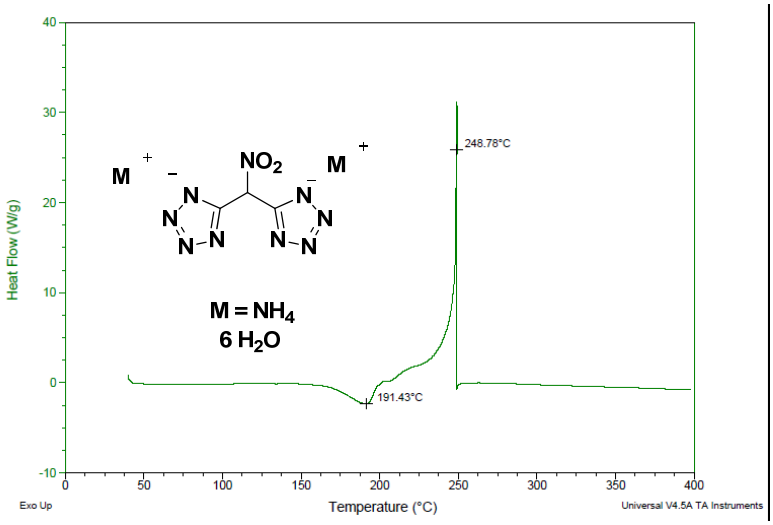


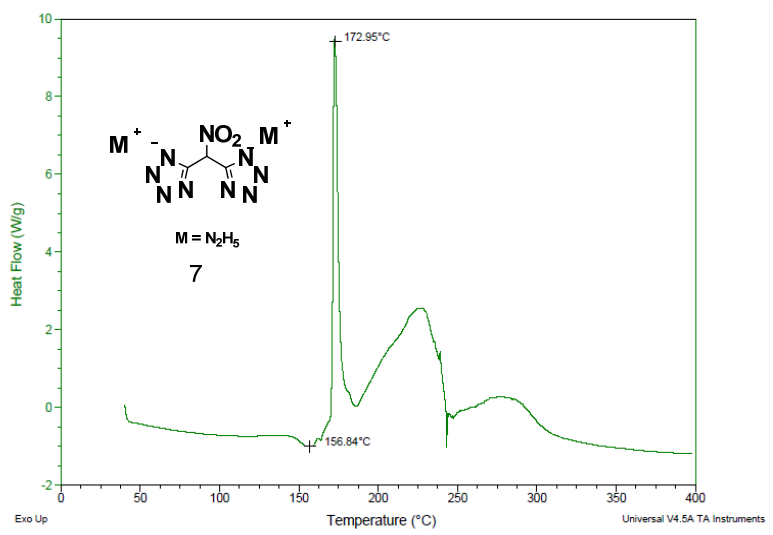
Figure S1 ^{15}N NMR spectrum of **2.**

DSC scans for 2, 3, 6, 7 – 10.









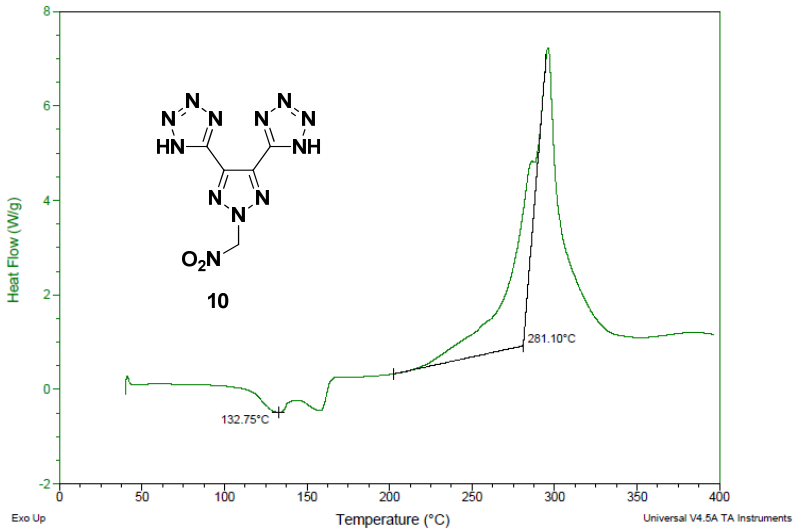


Figure S2 DSC curves of **2, 3, 6, 7 ,10.**

Reference

S1 D. Chand, D. A. Parrish. J. M. Shreeve. *J. Mater. Chem. A*. **2013**, *1*, 15383–15389.