

Supplementary Information

General methods:

Melting points T_m and decomposition points T_{dec} were measured with a Perkin-Elmer Pyris6 DSC (T_{onset}), using a heating rate of 5 °C min⁻¹ and checked by a Büchi Melting Point B-540 apparatus. Infrared spectra were measured with a Perkin-Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device, Raman spectra were recorded with a Perkin-Elmer 2000 NIR FT spectrometer fitted with a Nd:YAG laser ($\lambda = 1064$ nm). NMR spectra were recorded in anhydrous diethyl ether and at ambient temperature with a JEOL Eclipse 400 instrument and chemical shifts were determined with respect to external Me₄Si (¹³C, 100.5 MHz) and MeNO₂ (¹⁴N, 28.9 MHz). Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (DCI+). Analysis of C/N contents were performed with an Elemental Vario Micro Analyzer.

For compound **2** an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo- K_α radiation ($\lambda = 0.71073$ Å). The data collection was realized by using CRYSDISP software. The structures were solved by direct methods using SIR97 and refined by full-matrix least-squares on F^2 (SHELXL-97). All atoms were refined anisotropically. DIAMOND plots are shown with thermal ellipsoids at the 50 % probability level. Crystallographic data (excluding structure factors) for the reported structure in this communication has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-963150 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Synthesis of TNM₂-BOD (**2**):

To a solution of NO₂BF₄ (200 mg, 1.50 mmol) in anhydrous acetonitrile at -10 °C was added compound **1** (250 mg, 0.66 mmol) in small portions over a period of 10 minutes. The reaction mixture was stirred for one hour at 0 °C and the solvent removed under reduced pressure. The remaining yellowish solid was extracted with warm Et₂O (50 mL), solids were filtrated and the solvent concentrated under reduced pressure to about 3 mL yielding a crystalline solid at 8 °C overnight. The solvent was removed furnishing compound **2** (80 mg, 0.18 mmol, 27 %) as colourless crystals.

DSC (5 °C min⁻¹, T_{onset}): $T_{melt} = 119$ °C, $T_{dec} = 124$ °C; **IR**: $\tilde{\nu} = 1710$ (w), 1608 (s), 1561 (m), 1405 (w), 1347 (w), 1291 (m), 1271 (s), 1227 (s), 1139 (s), 1072 (s), 1038 (s), 975 (m), 962 (m), 933 (m), 904 (s), 839 (s), 792 (s), 725 (m), 668 (m), 656 (m) cm⁻¹; **Raman** (1064 nm, 200 mW, 25 °C): $\tilde{\nu} = 1621$ (23), 1595 (100), 1573 (45), 1415 (32), 1349 (8), 1294 (10), 1275 (11), 1097 (4), 1023 (11), 960 (29), 933 (16), 844 (45), 799 (4), 769 (5), 627 (7), 518 (12) cm⁻¹; **¹³C NMR** (68 MHz, anh. Et₂O): $\delta = 163.8$ (OCN), 160.2 (CC), 117.8 (C(NO₂)₃) ppm; **¹⁴N NMR** (29 MHz, anh. Et₂O): $\delta = -35$ (NO₂) ppm; **m/z** (DCI+): 437.3 [M+H]⁺;

EA: found C, 16.67, N, 32.33. C₆N₁₀O₁₄ requires C, 16.52, N, 32.12 %; **impact sensitivity**: 10 J; **friction sensitivity**: 80 N; **grain size**: <100 µm.

Crystallographic data of TNM₂-BOD (**2**):

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Name	TNM ₂ -BOD
Sum formula	C ₆ N ₁₀ O ₁₄
formula weight / g cm ⁻³	436.12
crystal dimensions / mm	0.50 × 0.33 × 0.03
crystal description	colourless plate
crystal system	monoclinic
space group	$P 2_1/c$
$a / \text{Å}$	10.6840(5)
$b / \text{Å}$	5.8606(3)
$c / \text{Å}$	23.5393(11)
$\alpha / ^\circ$	90.0
$\beta / ^\circ$	102.936(5)
$\gamma / ^\circ$	90.0
$V / \text{Å}^3$	1436.50(12)
Z	4
$\rho_{\text{calc}} / \text{g cm}^{-3}$	2.017
μ / mm^{-1}	0.200
$F(000)$	872
temperature / K	100(2)
θ range / °	4.18–26.37
index ranges	-13 ≤ h ≤ 13 -7 ≤ k ≤ 7 -29 ≤ l ≤ 29
reflections measured	20654
reflections independent	2909
reflections unique	2515 ($R_{int} = 0.0391$)
$R1, wR2$ (2 σ data)	0.0423, 0.0929
$R1, wR2$ (all data)	0.0505, 0.0966
data/restraints/parameters	2909/0/271
GoF on F^2	1.145
residual electron density	-0.240/0.328
Irradiation / Å	MoK α 0.71073
Device type	Oxford XCalibur3
Adsorption correction	multi-scan
CCDC deposit number	963150