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Fully C/N-Polynitro-Functionalized 2,2′-Biimidazole Derivatives as Nitrogen- and Oxygen-Rich Energetic Salts

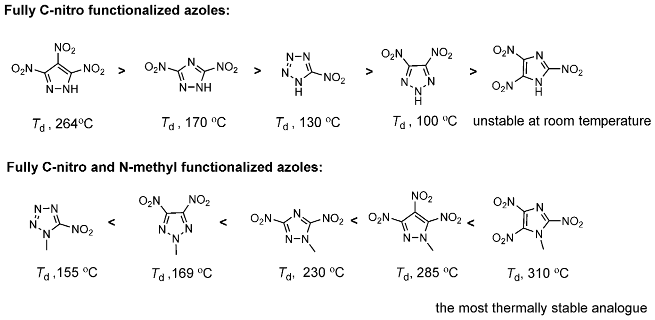
Ping Yin, Chunlin He, and Jean’ne M. Shreeve*[a]

Abstract: Through the use of a fully C/N-functionalized imidazole-based anion, it was possible to prepare nitrogen- and oxygen-rich energetic salts. When *N*,*N*-dinitramino imidazole was paired with nitrogen-rich bases, versatile ionic derivatives were prepared and fully characterized by IR, and ^{1}H, and ^{13}C NMR spectroscopy and elemental analysis. Both experimental and theoretical evaluations show promising properties for these energetic compounds, such as high density, positive heats of formation, good oxygen balance, and acceptable stabilities. The energetic salts exhibit promising energetic performance comparable to the benchmark explosive RDX (1,3,5-trinitrotriazacyclohexane).

Introduction

Nitrogen-rich heterocycles are one of the most important structural motifs in the design of high energy density materials (HEDMs).[1] Due to practical application demands, the interest of researchers is focused mainly on density, heat of formation, oxygen balance, detonation properties, thermal stability, and sensitivity toward destructive stimuli.[2] However, investigation involving diverse HEDMs continues to demonstrate the contradictory nature of energetic performance and molecular stability. As such, understanding of rational molecular design is crucial to achieve an ideal balance for different criteria. In general, introduction of highly energetic functionalities (for example nitro, azido, diazo, N-oxide, and trinitromethyl) are capable of improving density and detonation properties.[2c,3] Meanwhile, clever formation of versatile interactions between different energetic moieties are conducive in retaining a certain molecular stability.[4]

Recently, the development of N-heterocyclic chemistry has led to an upsurge of five membered azole-based energetic materials.[5] The advanced energetic properties benefit not only from the positive heat of formation of the nitrogen-rich backbone, but also from the electron-rich features that are compatible with multiple energetic functionalities. Reflecting on the progress in azole-based energetic materials, fully C-nitrated functionalization appears to be the mainstream strategy toward high energetic performance (Scheme 1).



Scheme 1. Thermal stability of fully C-nitrated azoles and their N-methyl functionalized derivatives.

Among these analogues, 2,4,5-trinitro-1*H*-imidazole (TNI), albeit with a high predicted density of 1.905 g cm^{-3},[6] is not isolable neat and can only be stored in ether solution.[7] In comparison, the other fully C-nitrated azoles exhibit moderate to good decomposition temperatures ranging from 100 to 264 °C.[8] In contrast N-methyl functionalization of fully C-nitrated azoles enhances greatly the thermal stability where the *N*-methyl-2,4,5-trinitro-1*H*-imidazole at 310 °C has the highest decomposition temperature of the N-methyl functionalized derivatives;[9] furthermore, ammonium trinitroimidazolate is more thermally stable than other ammonium azolates.[10]

This unique structure–property feature indicates that it is possible to balance energetic performance and stability by virtue of both C- and N- functionalizations. Despite unsuccessful attempts to stabilize a form of TNI, research enthusiasm is still increasing in the search for imidazole-based HEDMs.[11] Recently, a multifunctionalized strategy to improve the energetic performance of various heterocyclic backbones, such as pyrazole, triazole, and imidazole, was demonstrated. Of these, representative compounds include 5-nitramino-3,4-dinitropyrazole (NADNP) and *N*,*N*′-dinitramino-4,4′,5,5′-tetranitro-bisimidazole (**4**) with excellent detonation properties that are superior to those of cyclo-1,3,5,7-tetramethylenene-2,4,6,8-tetranitramine (HMX).[4e,f] However, their relatively high sensitivities may preclude practical application. In the continuing research interest in exploring energetic materials, various energetic bisimida-

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[a] Dr. P. Yin, Dr. C. He, Prof. Dr. J. M. Shreeve
Department of Chemistry, College of Science, University of Idaho
P.O. Box 442343, Moscow, 83844-2342 ID (USA)

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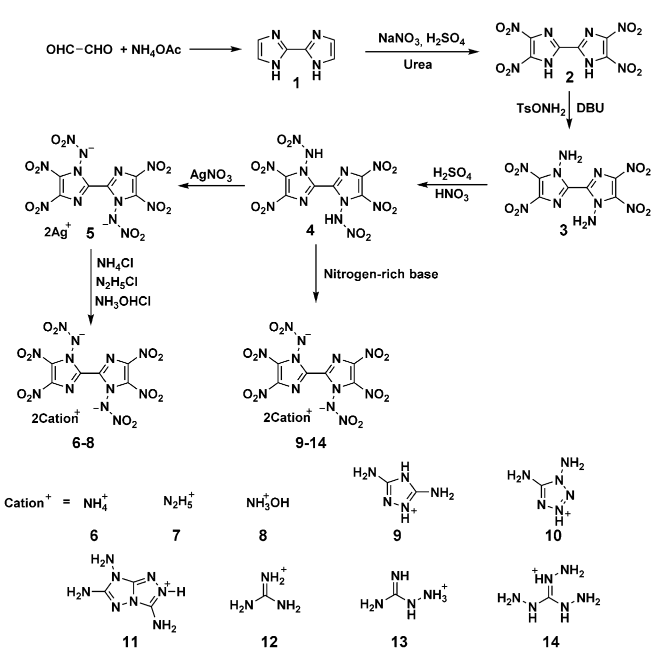
zole-based energetic salts were synthesized and further study associated with physicochemical properties indicate that they have favorable detonation properties with enhanced stabilities. Additionally, single-crystal X-ray crystallographic analysis was employed to acquire insight into structural features of the energetic salts.

Results and Discussion

The precursor 1*H*,1′*H*-2,2′-biimidazole (**1**) was prepared from glyoxal and ammonium acetate in water (Scheme 2). Employing sodium nitrate and concentrated sulfuric acid, nitration of carbon was accomplished.[12] Although *N*-nitro-functionalized biimidazole has been predicted as a high-performance compound exceeding HMX,[13] a stable form cannot be isolated due to the high sensitivity. In contrast, *N*-nitramino functionalized biimidazole was readily obtained by N-amination of **2** followed by the nitration of **3** using *O*-tosylhydroxylamine and H_2SO_4/HNO_3, respectively. A modified workup procedure by recrystallization of the crude *N*-amino product resulted in a good yield of highly pure **3** and precluded chromatographic column separation.[14] Because of the highly reactive nature of the *N*-amino groups, the nitration reaction of **3** in mixed acid was carried out at −15 to −10 °C to prevent N–N bond cleavage. Treated with potassium carbonate and silver nitrate, **4** was converted into the disilver salt, **5**. The following metathesis reactions with corresponding chloride salts gave rise to diammonium (**6**), dihydrazinium (**7**), and dihydroxylammonium (**8**) salts. Similarly, reaction of **4** with versatile nitrogen-rich bases yielded ionic derivatives, **9**–**14**. All of the new biimidazole-based energetic compounds were fully characterized by NMR and IR spectroscopy, thermal stability, elemental analyses, and impact and friction sensitivity.



Scheme 2. Synthesis of *N*,*N*′-nitroamino 4,4′,5,5′-tetranitro-2,2′-biimidazole (**4**) and its energetic salts (**6**–**14**).

For the *N*,*N*′-diamino compound (**3**), the characteristic IR absorption bands of NH_2 were observed as sharp double peaks at 3337 and 3325 cm^{-1}. Typically for polynitro compounds, the characteristic IR absorption bands of the nitro groups appeared in the 1300–1600 cm^{-1} region. The chemical shifts of the imidazole ring in the ^{13}C NMR spectra of **4** were found at 135.8, 132.4, and 129.0 ppm, which are very similar to those of ammonium salt (**6**) at 133.5, 132.1, and 128.7 ppm. Although the synthesis of **4** and **8** was studied previously, the detail data of ^{14}N and ^{15}N NMR spectra were not illustrated.[4f] The ^{14}N NMR spectra of the dinitroamino compound (**4**) and hydroxylammonium salt (**8**) were measured in [D$_6$]acetone and [D$_6$]DMSO, respectively (Figure 1). In the case of compound **4**, the resonance at −30.04 ppm can be assigned to the *N*-NO_2 group, whereas the resonances at −34.59 ppm and −38.49 ppm were attributed to the *C*-NO_2 groups on the basis of comparison with previously reported data.[4e]

Although the neat compound (**4**) can be stored for an extended period, a concentrated solution of **4** in [D$_6$]acetone was unstable for 24 h, precluding the acquisition of ^{15}N spectroscopic data. In the ^{14}N NMR spectrum of hydroxylammonium salt (**8**), three broad peaks are found at −5.20 (N4), −34.60 (N6), and −304.23 (N7). Whereas in the ^{15}N NMR spectrum of **8** five signals at −6.14 (N4), −26.66 (N5), −34.70 (N6), −128.06 (N3), −135.26 (N2) are seen.

Aiming for structural insight, **12** was further characterized by single-crystal X-ray diffraction (Figure 2).[15] A crystal of **12** was obtained by dissolving **12** in methanol and allowing chloro-

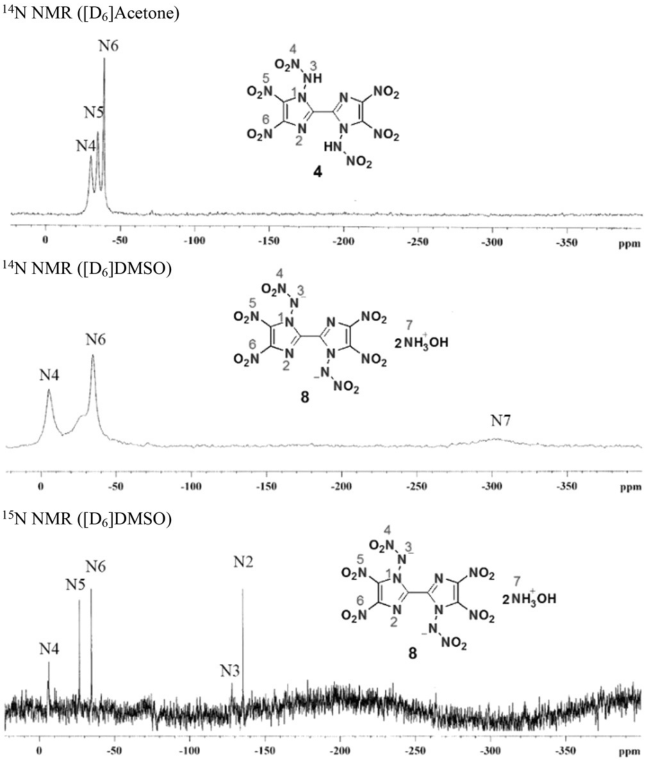


Figure 1. ^{14}N and ^{15}N NMR spectra of **4** and **8**.

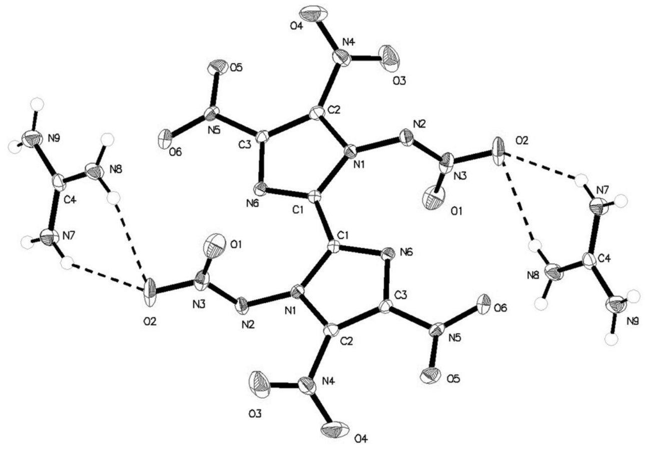


Figure 2. Single-crystal X-ray structure of **12**.

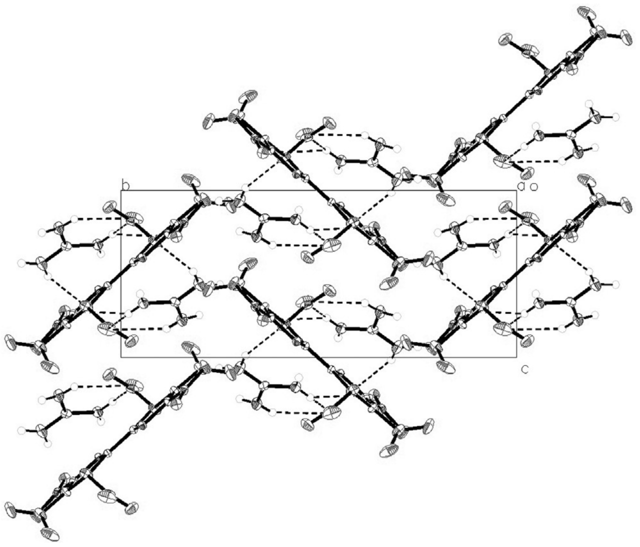


Figure 3. Packing diagram of **12** along the *a* axis.

form to diffuse into the solution. With a calculated density of 1.813 g cm^{-3} at 100 K, **12** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell (Figure 3). Compared to some reported guanidinium salts, for example guanidinium nitrate (**15**) and guanidinium dinitramide (**16**), salt **12** shows a higher density arising from the C/N- fully polynitro functionalized anion (**12**, 1.813 g cm^{-3} at 100 K, 1.75 g cm^{-3} at 298 K; **15**, 1.369 g cm^{-3} at 291 K; **16**, 1.673 g cm^{-3} at 293 K).[16] The C–N bond lengths of four C-nitro groups are similar (N4–C2 1.441(2) Å, N5–C3 1.438(2) Å). Generally, nitro groups play a role as hydrogen-bond acceptors. Hydrogen-bond interactions of **12** are found between the guanidinium cations and N-nitramino anions (N7–H7A···O2, N8–H8A···O2, N7–H7A···O6, and N9–H9A···O2).

To evaluate the thermal stability, differential scanning calorimetric (DSC) measurements were used for the biimidazole-based energetic compounds (**3**, **4**, and **6**–**14**) (Table 1). The *N*,*N*-diamino compound **3** has a decomposition temperature (T_d) of 217 °C comparable to that of RDX (T_d, 205 °C). In spite of the low decomposition temperature of the *N*,*N*-dinitroamine (**4**) (T_d, 116 °C), the energetic salts of **4** (**6**–**14**) have moderate to good thermal stabilities with decomposition temperatures ranging between 113 °C and 203 °C. When 3,6,7-triamino-7H-[1,2,4]triazolo[5,1-*c*][1,2,4]triazole was utilized as a nitrogen-rich base, the resulting salt (**11**) is the most thermally stable of these energetic salts (203 °C).

As a pivotal evaluation, densities of these new energetic compounds were measured with a gas pycnometer at room temperature. The measured densities (*d*) of these energetic salts (**6**–**14**) fall between 1.75 and 1.85 g cm^{-3} (Table 1). Impact and friction sensitivities of biimidazole-based energetic compounds were measured using a BAM drop hammer apparatus and a BAM friction tester, respectively. Compound **3** shows moderately sensitive parameters with an impact sensitivity (IS) of 15 J and a friction sensitivity (FS) of 160 J. In spite of the relatively sensitive characteristics of **4** (IS, 3 J; FS, 20 N), its ionic derivatives exhibit lower impact and friction sensitivities (IS, 5-30 J; FS, 60-240 N).

Theoretical computations associated with the heats of formation (ΔH_f) were performed by using the Gaussian 03 (Revision D.01) suite of programs.[17] As seen in Table 1, energetic

Table 1. Properties of biimidazole-based energetic compounds **3**, **4**, and **6**–**14**.

Comp	T_d[a] [°C]	d[b] [g cm^{-3}]	ΔH_f[c] [kJ g^{-1}]	P[d] [GPa]	v_D[e] [m s^{-1}]	IS[f] [J]	FS[g] [N]	OB[h] [%]
3	217	1.93	0.90	36.6	9012	15	160	0
4[i]	116	1.94	1.11	40.1	9350	3	20	18.4
6	135	1.78	0.75	33.6	8715	8	80	4.71
7	128	1.79	1.33	35.7	8916	5	80	3.21
8[i]	135	1.85	0.90	38.2	9169	6	80	12.8
9	113	1.78	1.19	30.4	8499	30	240	−12.7
10	133	1.80	2.45	35.4	8996	5	60	−2.52
11	203	1.85	1.96	33.8	8899	10	120	−15.1
12	158	1.75	0.59	29.5	8409	30	240	−5.80
13	141	1.81	0.95	33.0	8786	25	160	−8.25
14	140	1.77	1.55	32.8	8898	9	80	−12.5
RDX	205	1.81	0.36	34.9	8748	7.4	120	0

[a] Decomposition temperature. [b] Density measured by gas pycnometer (25 °C). [c] Heat of formation. [d] Detonation pressure (calculated with Explo5 v6.01). [e] Detonation velocity (calculated with Explo 6.01). [f] Impact sensitivity. [g] Friction sensitivity. [h] Oxygen balance (based on CO) for $C_aH_bO_cN_d$, $1600(c-a-b/2)/MW$, MW = molecular weight. [i] Ref. [4f].

biimidazoles and ionic derivatives are endothermic compounds with positive heats of formation ranging from 0.59 $kJ\,g^{-1}$ to 2.45 $kJ\,g^{-1}$, which exceed those of RDX (0.36 $kJ\,g^{-1}$) and HMX (0.36 $kJ\,g^{-1}$). Incorporating experimental densities and theoretically calculated heats of formation, the detonation pressures (P) and velocities (v_D) were calculated based on the EXPLO5 v6.01 program.[18] With high densities and favorable heats of formation, the detonation properties of **3** ($P=36.6$ GPa; $v_D=9012\,m\,s^{-1}$) and **4** ($P=40.1$ GPa; $v_D=9350\,m\,s^{-1}$) suggest their potential use as high explosives. Further to molecular compounds **3** and **4**, the ionic derivatives also show promising detonation parameters ($P=29.5$–38.2 GPa; $v_D=8409$–$9169\,m\,s^{-1}$). Among them, **11** exhibits favorable overall properties, such as density, detonation properties, and molecular stabilities, which are comparable to the benchmark explosive RDX (**11**: $d=1.85\,g\,cm^{-3}$, $P=33.8$ GPa, $v_D=8899\,ms^{-1}$, $T_d=203\,^{\circ}C$, IS = 10 J, FS = 120 N; RDX: $d=1.81\,g\,cm^{-3}$, $P=34.9$ GPa, $v_D=8748\,m\,s^{-1}$, $T_d=205\,^{\circ}C$, IS = 7 J, FS = 120 N).

Oxygen balance (OB) is a significant index to indicate the deficiency or excess of oxygen in energetic ingredients. While **4**, **6**, **7**, and **8** have positive oxygen balances (3.21 to 18.4), **3** has an OB value of zero, and the other compounds show negative values (-2.52 to -15.1). Arising from fully *C*- and *N*-polynitro functionalization, the nitrogen- and oxygen-rich compounds **4** and **8** exhibit promising OB values of 18.4 and 12.8, respectively, which suggests use as potential energetic oxidizers to improve the overall performance in multiple energetic ingredients.

Conclusion

A reasonable assembly of *C*-nitro and *N*-nitroamino functionalities gave rise to a family of new high-density energetic biimidazoles. All biimidazole-based compounds were fully characterized by elemental analysis and IR and NMR spectroscopy. Compared to the instability of the fully C-nitrated monocyclic imidazole TNI, polynitro functionalized biimidazole **4** and its energetic salts exhibit enhanced molecular stability and performance parameters, such as density, oxygen balance, and detonation properties, are superior to those of TNI. Based on both experimental and calculated methods, some representative energetic salts exhibit promising properties, such as good densities, high detonation parameters, and moderate sensitivities. By incorporating a conventional *C*-nitro functionality and a novel *N*-nitroamino functionality into biimidazole rings, this enriches the design strategy of polynitro introduction and demonstrates a promising pathway to high-density energetic heterocycles.

Experimental Section

General methods

All chemicals were pure analytical grade materials obtained from Aldrich, Acros Organics, or AK Scientific and used as received. Decomposition points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q10) at a scan rate of 5 °C min^{-1}. ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) or 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts are reported relative to Me_4Si or deuterated solvents. Elemental analyses (C, H, N) were performed on a CE-440 Elemental Analyzer. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester. IR spectra were recorded using KBr pellets with a Biorad Model 3000 FTS spectrometer. Densities were determined at 25 °C by employing a Micromeritics AccuPyc 1330 gas pycnometer.

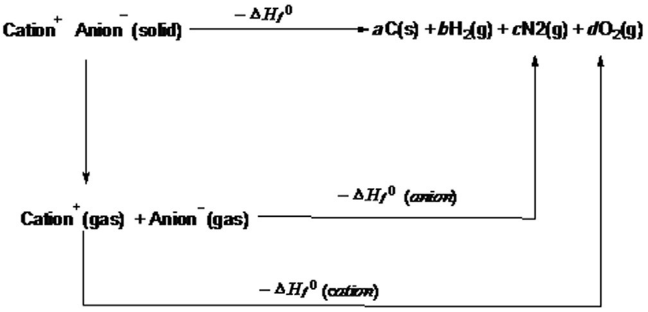
Theoretical study

Based on the method of isodesmic reactions, the gas-phase enthalpies of formation were computed and the enthalpy of reaction is obtained by combining the MP2/6–311^{++}G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (HT), and other thermal factors.[17] Thus, the gas phase enthalpy of the species can be extracted. Solid-state heats of formation of the resulting compounds were calculated with Equation (1) (T_m is the melting temperature).[19]

$$\Delta H_f = \Delta H_f(g) - \Delta H_{sub} = \Delta H_f(g) - 188\,[\mathrm{J\,mol^{-1}\,K^{-1}}] \times T_m \qquad (1)$$

Based on the Born–Haber energy cycle (Scheme 3), the solid phase heat of formation of energetic salts can be simplified by Equation (2).

$$\begin{aligned} &\Delta H_f^{\circ}\,(\mathrm{salt, 298\,K}) = \\ &\Delta H_f^{\circ}\,(\mathrm{cation, 298\,K}) + \Delta H_f^{\circ}\,(\mathrm{anion, 298\,K}) - \Delta H_L \end{aligned} \qquad (2)$$



Scheme 3. Born–Haber cycle for the formation of biimidazole compounds. *a*, *b*, *c*, *d* are the number of moles of the respective products.

In Equation (2), the lattice energy (ΔH_L) could be predicted by using the formula suggested by reported methods [Equation (3)].[20]

$$\Delta H_L = U_{POT} + [p(n\mathrm{M}/2-2) + q(n_X/2-2)]\mathrm{RT} \qquad (3)$$

in which nM and n_X depend on the nature of the ions M^{p+} and X^{q-}, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form [Equation (4)]:

$$U_{POT}\,[\mathrm{kJ\,mol^{-1}}] = \gamma(\rho/M)_{1/3} + \delta \qquad (4)$$

4,4′,5,5′-tetranitro-1*H*,1′*H*-[2,2′-biimidazole]-1,1′-diamine (3): Preparation of 4,4′,5,5′-tetranitro-1H,1′H-2,2′-biimidazole dihydrate (**2**) was based on the modified method.[14] A mixture of **2** (4 mmol, 1.4 g) and 1,8-diazabicycloundec-7-ene (8 mmol, 1.22 g) in CH_3CN (20 mL) was stirred at room temperature for 1 h. To this orange suspension, freshly prepared *O*-tosylhydroxylamine (ca. 15 mmol) in chloroform solution (30 mL) was added in 2 min. The final mixture was stirred for 3 h and then was filtered, washed by CH_3CN (3×5 mL). The combined filtrate was concentrated and the final crude product was recrystallized in ethanol and water to yield **3** (orange solid, 63% yield). ^1H NMR (CD_3CN): $\delta = 6.30$ ppm (s, 4H); ^{13}C NMR (CD_3CN): $\delta = 137.0, 134.8, 131.6$ ppm; elemental analysis (%) calcd for $C_6H_4N_{10}O_8$ (344.16): C 20.94, H 1.17, N 40.70; found: C 21.14, H 1.21, N 39.97.

Disilver *N*,*N*′-(4,4′,5,5′-tetranitro-1*H*,1′*H*-[2,2′-biimidazole]-1,1′-diyl)dinitramide (5): The dinitramino compound **4** was prepared according to our previous method.[4f] Potassium carbonate (138 mg, 1 mmol) was added to a solution of **4** (434 mg, 1 mmol) in distilled water (2 mL) and the mixture was stirred at room temperature for 10 min. Then silver nitrate (340 mg, 2 mmol) was added to the suspension and stirred at room temperature for 1 h. The precipitate **5** was collected by filtration and dried in vacuum (orange solid, 95%). Elemental analysis (%) calcd for $C_6N_{12}O_{12}Ag_2$ (647.87): C 11.12, H 0.00, N 25.94; found: C 11.47, H 0.26, N 26.40.

General procedure for salts 6–8: Compound **5** (648 mg, 1 mmol) was added to an ice-cold methanol solution (10 mL) of ammonium chloride (107 mg, 2 mmol), hydrazinium chloride (137 mg, 2 mmol), or hydroxylammonium chloride (139 mg, 2 mmol). After stirring 1 h at 0–5 °C, silver chloride was removed by filtration and washed with a small amount of methanol. The filtrate was concentrated under reduced pressure and dried in vacuo to yield **6**–**8**.[4f]

Diammonium *N*,*N*′-(4,4′,5,5′-tetranitro-1*H*,1′*H*-[2,2′-biimidazole]-1,1′-diyl)dinitramide dihydrate (6): red solid, 86% yield. ^1H NMR ([D$_6$]DMSO): $\delta = 7.08$ ppm (br, 8H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 135.5, 132.1, 128.7$ ppm; IR (KBr pellet): $\tilde{\nu} = 3554, 1631, 1536, 1440, 1413, 1302, 1279, 1109, 853, 810, 717$ cm^{-1}; elemental analysis (%) calcd for $C_6H_{12}N_{14}O_{14}$ (504.25): C 14.29, H 2.40, N 38.89; found: C 14.60, H 2.16, N 37.23.

Dihydrazinium *N*,*N*′-(4,4′,5,5′-tetranitro-1*H*,1′*H*-[2,2′-biimidazole]-1,1′-diyl)dinitramide (7): red solid, 82% yield. ^1H NMR (CD_3CN): $\delta = 4.43$ ppm (br, 10H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 135.5, 132.1, 128.7$ ppm; IR (KBr pellet): $\tilde{\nu} = 3375, 3303, 3159, 2154, 1626, 1546, 1422, 1279, 1090, 928, 851, 806, 768$ cm^{-1}; elemental analysis (%) calcd for $C_6H_{10}N_{16}O_{12}$ (498.25): C 14.46, H 2.02, N 44.98; found: C 15.09,H 2.17, N 42.70.

General procedure for salts 9–14: Compound **4** (434 mg, 1 mmol) was added to a mixture of 3,5-diaminotriazole (198 mg, 2 mmol) in MeOH (10 mL), 1,5-diaminotetrazole (200 mg, 2 mmol) in MeOH (10 mL), 3,6,7-triamino-7*H*-[1,2,4]triazolo[5,1-*c*][1,2,4]triazole (308 mg, 2 mmol) in H_2O (15 mL), guanidinium carbonate (180 mg, 1 mmol) in MeOH (10 mL), aminoguanidinium carbonate (272 mg, 2 mmol) in MeOH (10 mL), or triaminoguanidinium chloride (280 mg, 2 mmol) in EtOH (20 mL) and H_2O (5 mL). After stirring 1 h at 50 °C, the product was obtained by filtration or concentration.

Di(3,5-Diamino-triazolium) *N*,*N*′-(4,4′,5,5′-tetranitro-1H,1′H-[2,2′-biimidazole]-1,1′-diyl)dinitramide (9): red solid, 93% yield. ^1H NMR ([D$_6$]DMSO): $\delta = 7.00$ ppm (br, 8H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 152.8, 135.5, 132.1, 128.7$ ppm; IR (KBr pellet): $\tilde{\nu} = 3310, 1765, 1695, 1655, 1418, 1292, 1111, 1057, 1015, 850, 804, 776$ cm^{-1}; elemental analysis (%) calcd for $C_{10}H_{12}N_{22}O_{12}$ (632.35): C 18.99, H 1.91, N 48.73; found: C 18.62, H 1.89, N 47.51.

Di(1,5-diamino-tetrazolium) *N*,*N*′-(4,4′,5,5′-tetranitro-1*H*,1′*H*-[2,2′-biimidazole]-1,1′-diyl)dinitramide (10): red solid, 91% yield. ^1H NMR ([D$_6$]DMSO): $\delta = 5.25$ ppm (br, 8H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 153.0, 135.6, 132.2, 128.8$ ppm; IR (KBr pellet): $\tilde{\nu} = 3433, 3154, 2745, 2155, 1759, 1701, 1649, 1542, 1425, 1383, 1298, 1043, 864, 809, 781$ cm^{-1}; elemental analysis (%) calcd for $C_8H_{10}N_{24}O_{12}$ (634.32): C 15.15, H 1.59, N 53.00; found: C 14.72, H 1.67, N 50.93.

Di[3,6,7-triamino-7*H*-[1,2,4]triazolo[5,1-*c*][1,2,4]triazol-2-ium] *N*,*N*′-(4,4′,5,5′-tetranitro-1*H*,1′*H*-[2,2′-biimidazole]-1,1′-diyl)dinitramide (11): yellow solid, 85% yield. ^1H NMR ([D$_6$]DMSO): $\delta = 13.32$ (br, 1H), 8.16 (s, 2H), 7.21 (s, 2H), 5.76 ppm (s, 2H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 153.0, 135.6, 132.2, 128.8$ ppm; IR (KBr pellet): $\tilde{\nu} = 3429, 3364, 3297, 3158, 1699, 1645, 1542, 1414, 1299, 1042, 852, 810, 702$ cm^{-1}; elemental analysis (%) calcd for $C_{12}H_{14}N_{28}O_{12}$ (742.43): C 19.41, H 1.90, N 52.83; found: C 19.12, H 1.86, N 52.13.

Di(guanidinium) *N*,*N*′-(4,4′,5,5′-tetranitro-1*H*,1′*H*-[2,2′-biimidazole]-1,1′-diyl)dinitramide (12): yellow solid, 81% yield. ^1H NMR ([D$_6$]DMSO): $\delta = 6.90$ ppm (s, 12H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 158.0, 135.5, 132.1, 128.8$ ppm; IR (KBr pellet): $\tilde{\nu} = 3455, 3353, 1655, 1524, 1427, 1379, 1349, 1302, 1154, 1061, 1000, 850, 806$ cm^{-1}; elemental analysis (%) calcd for $C_8H_{12}N_{18}O_{12}$ (552.30): C 17.40, H 2.19; N 45.65; found: C 17.48; H 2.19; N 45.05.

Di(aminoguanidinium) *N*,*N*′-(4,4′,5,5′-tetranitro-1*H*,1′*H*-[2,2′-biimidazole]-1,1′-diyl)dinitramide (13): yellow solid, 75% yield. ^1H NMR ([D$_6$]DMSO): $\delta = 8.54$ (s, 2H), 7.20 (br, 4H), 6.75 (br, 4H), 4.67 ppm (s, 4H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 158.7, 135.4, 132.0, 128.6$ ppm; IR (KBr pellet): $\tilde{\nu} = 3439, 3362, 1672, 1549, 1427, 1382, 1359, 1290, 1197, 1059, 951, 916, 849, 806, 774, 664$ cm^{-1}; elemental analysis (%) calcd for $C_8H_{14}N_{20}O_{12}$ (582.33): C 16.50, H 2.42, N 48.11; found: C 16.48, H 2.51, N 47.97.

Di(triaminoguanidinium) *N*,*N*′-(4,4′,5,5′-tetranitro-1*H*,1′*H*-[2,2′-biimidazole]-1,1′-diyl)dinitramide (14): yellow solid, 63% yield. ^1H NMR ([D$_6$]DMSO): $\delta = 8.57$ (s, 6H), 4.48 ppm (s, 12H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 159.0, 135.4, 132.0, 128.6$ ppm; IR (KBr pellet): $\tilde{\nu} = 3360, 3213, 3147, 3071, 1527, 1442, 1371, 1348, 1304, 1285, 1272, 1208, 1136, 1051, 1017, 989, 964, 927, 863, 848, 811, 777, 757, 639, 616$ cm^{-1}; elemental analysis (%) calcd for $C_8H_{18}N_{24}O_{12}$ (642.39): C 14.96, H 2.82, N 52.33; found: C 14.52, H 3.13, N 53.07.

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