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Conjugated Energetic Salts Based on 3,3'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(2,4,6-trinitrophenol)

Junhui Xu, Jianping Wei, Fangmei Li, Qingguo Ma and Xinhua Peng*

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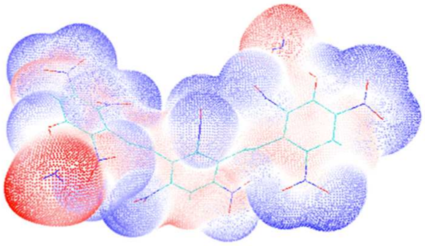

Highly conjugated energetic salts exhibit remarkable thermostability and insensitivity.

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Conjugated Energetic Salts Based on 3,3'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(2,4,6-trinitrophenol) †

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Based on a design strategy that has resulted in conjugated energetic materials, 3,3'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethane-2,1-diyl))bis(2,4,6-trinitrophenol) and its nitrogen-rich salts were obtained and characterized via spectral and elemental analyses. These new molecules exhibit good thermal stability (T_d = 268.4–311.3 ℃), especially for hydrazinium salt **4c**, which is comparable to that of the benchmark HNS. Also, they present low impact sensitivity (> 40 J), high density (1.67–1.88 g cm^{-3}), acceptable detonation properties (7268–8527 m s^{-1}, 26.7–34.1 GPa) and brisance parameters (103.9–144.4). The energetic properties of the salts suggests potential applications to new energetic materials.

Introduction

Energetic materials form an integral part of weapon systems as well as a large number of new high energy density materials (HEDMs) including thermally stable explosives, high-performance explosives, melt-castable explosives, insensitive high explosives and energetic binders have been reported in the literature in recent years.[1] Synthesis chemists are combining their long-held expertise in manipulating atoms and molecules with physical scientists and engineers to create materials with designed functions. Much effort has been expended to meet the main challenge of the desired combination of large energy content with maximum possible chemical stability to ensure safe synthesis and handling.[2] Energetic materials are experiencing tremendous growth to meet the increasing demand for high-performing materials with high thermal and mechanical stability in the last decades.[3] In the quest for higher detonation performance and lower sensitivity, energetic salts have gradually become a popular choice, as these salts possess low volatility, high thermal stability. Also, energetic salts with readily modified properties are usually formed in a simple synthesis process. This provides a powerful methodology for the design and synthesis of HEDMs for specific purposes.

Recently, polynitro azoles have attracted more and more attention due to their advantages of high detonation performance based on the presence of polynitro groups and high-nitrogen content.[4] Unfortunately, compounds in this category also appear to have limits, which include high impact sensitivity and low decomposition temperature in particular.[4b, 5] Nitroaromatic compounds (e.g. hexanitrostilbene (HNS) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)) as traditional energetic materials, have received special attention because of their ability to withstand the high temperatures.[6] (Figure 1) The examples of imparting higher thermal stability through the introduction conjugation and delocalization effects in explosive molecules are HNS and 1,1-diamino-2,2-dinitroethene (FOX-7). Based on structure-performance relationships, introduction of conjugation effects can improve the thermal stability of explosive molecules.[1b] Our aimed design was a combination of conjugation and more nitro groups. The presence of nitro groups tends to decrease the heat of formation, but contributes greatly to the overall energetic performance. Also, the nitro group enhances the oxygen balance and density, which improves the detonation performances (pressure and velocity).[7] Conventionally, nitroaromatic compounds such as 2,4,6-trinitrotoluene (TNT) and TATB produce energy mainly from the combustion of the carbon backbone, while consuming the oxygen provided by the nitro groups.[3g, 8]

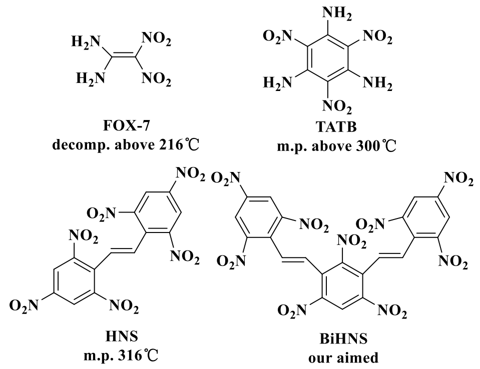

Fig. 1 Design of thermally stable energetic materials

In the continuing effort to seek more powerful, less sensitive, thermally stable energetic materials, we intended to extend the chemistry of BiHNS-like compounds.[9] The two C=C unsaturated double bonds were introduced by Knoevenagel condensation between 2,4,6-trinitro-*m*-xylene (TNMX) and two equivalents of aromatic aldehydes in boiling benzene with piperidine catalyzed. The condensed products with the expanding π-π conjugation effect facilitated the application. Since the performance of the energetic materials was affected by the introduction of additional energetic groups, further introduction of nitro groups into the benzene rings should be worthwhile. However, the electrophilic nitration of benzene rings in nitrostilbenes was generally accompanied by the oxidization of the C=C double bond.[10] Thereby the synthesis and isolation of such energetic materials with more nitro groups introduced and the

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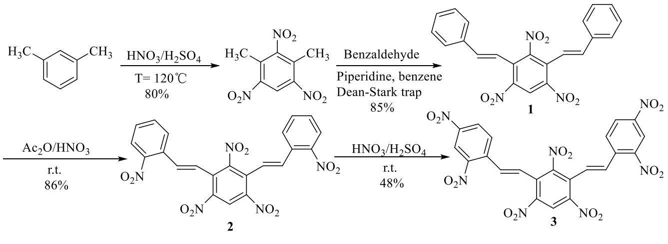
sound C=C double bond existed usually pose an interesting but challenging design strategy.

Since ((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))dibenzene (**1**) could not be nitrated to the nona-nitro derivative directly, an hydroxyl group, a strong electron donating substituent, was introduced into the *meta*-position of the unnitrated ring to enhance the reactivity of its *ortho-para* positions in a post nitration reaction. The strong electron-withdrawing effects of the nitro group could deprotonate hydroxyl to form energetic salts when paired with bases. To our knowledge, a few nitroaromatic anion-based energetic salts have been reported: energetic salts of picric acid[11], dipicrylamine[12] and trinitrophloroglucinol[13]. Our contribution thus lies in the synthesis of the previously unknown 3,3'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(2,4,6-trinitrophenol) (**4**) as well as its related ionic derivatives. The compounds were characterized using infrared, MS, multinuclear NMR spectroscopy and elemental analysis. The potential application of the synthesized compounds of energetic materials was studied and evaluated using the values obtained in our experiment for the thermal decomposition and the impact sensitivity data as well as the calculated performance characteristics.

Results and Discussion

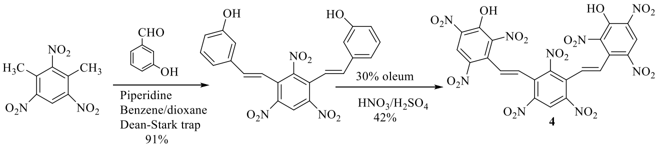
Synthesis

Initially, ((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl)) dibenzene (**1**) was selected as an precursor for the preparation of new energetic materials BiHNS. The generation of **1** from the Knoevenagel condensation between benzaldehyde and TNMX which was obtained from one-pot nitration of *m*-xylene at elevated temperatures in mixed acid. 2,2'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis- (ethene-2,1-diyl))bis(nitrobenzene) (**2**) was achieved with high selectivity in a solution of nitric acid and acetic anhydride at the room temperature. Then, nitration of **2** with concentrated sulfuric and fuming nitric acid yields 4,4'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(1,3-dinitro-benzene) (**3**) in acceptable yields (Scheme 1). However, initial nitration directly from **1** in mixed acid failed to afford the product **3**. A strong nitrating agent would lead to many by-products, although the reaction conducted at a low temperature. The pre-existing nitro groups in aromatic rings were advantageous by making the C=C double bonds less prone to oxidation. As more nitro groups were introduced, the C=C double bonds became more electron deficient and deactivated toward the electrophilic attack. Also, it was found that conducting the further nitration of **3** under different conditions, failed to give the final product BiHNS.



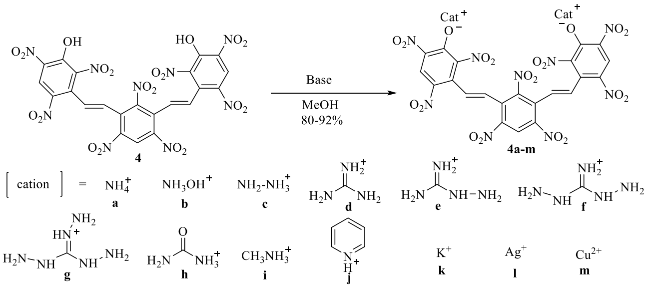
Scheme 1 Synthesis of 4,4'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene) bis(ethene-2,1-diyl))bis(1,3-dinitrobenzene)

Similarly, the synthesis of 3,3'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))diphenol from the direct condensation TNMX with 3-hydroxy-benzaldehyde in benzene solution with piperidine as catalyst was very difficult. Better results were obtained with 1, 4-dioxane as cosolvent and portionwise addition of piperidine. Phenolic substrates which undergo oxidative side reactions could also pose a serious problem. Sulfonic acid groups were electron withdrawing and moderated the nitration step as well as protected the substrate from oxidation. The condensation product 3,3'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1diyl))diphenol was heated on a steam bath with excess oleum before nitration. The two-steps sulfonation-nitration processes provided a versatile method for the synthesis of **4** and the carefully controlled temperature in this reaction was very important (Scheme 2).



Scheme 2 Synthesis of 3,3'-((1*E*,1'*E*)- (2,4,6- trinitro-1,3-phenylene)bis (ethene-2,1-diyl))bis (2,4,6-trinitrophenol)

The formation of the nitrogen- rich and metal salts (**4a−m**) was straightforward. A methanolic solution of the compound **4** was prepared, and two equiv of the corresponding nitrogen-rich base or metallic salts were added (Scheme 3). Due to the high solubility of **4** and the low solubility of compounds **4a−m** in methanol, all nitrogen-rich as well as metal ionic derivatives could be isolated in excellent yields and high purity.



Scheme 3 Synthesis of ionic derivatives based on the 3,3'-((1*E*,1'*E*)- (2,4,6-trinitro-1,3-phenylene) bis(ethene-2,1-diyl))bis(2,4,6-trinitrophenol) anion

Spectroscopy

All compounds were fully characterized by IR as well as multinuclear NMR spectroscopy, mass spectrometry, elemental analyses and differential scanning calorimetry. The NMR spectroscopic data of all the salts were collected in DMSO-d_6. ^1H NMR spectroscopic coupling signals assigned to -CH=CH- double bonds were about 16.60 Hz, which determined the (*E*)-configuration. Besides, the infrared spectrum exhibited a band around 970 cm^{-1} which refers to C-H deformation in trans -C=C-. For compound **4**, the position of the resonance bands for the protons in the middle of the benzene ring were observed as a singlet at 8.96 ppm and a signal at 8.74 ppm for the protons on both sides of the benzene rings in the low field. The signal for hydroxyl group occurred as a weak broad singlet at 8.27 ppm. In the ^{13}C NMR spectra, the signals at δ= 159.4, 149.1, 147.1, 147.0, 136.0, 130.4, 127.7, 127.7, 125.5, 123.8, 121.9 and 120.4 ppm.

The deprotonation of **4** with nitrogen-rich bases did not have a major effect on signal shifts in the ^{13}C NMR and ^{1}H NMR spectra. On the basis of the values of the chemical shifts of ammonium (**4a**), hydroxylamine (**4b**), hydrazine (**4c**), guanidine (**4d**), aminoguanidine (**4e**), diaminoguanidine (**4f**), triaminoguanidine (**4g**) and urea (**4h**) moieties, NH, NH_2, NH_2^+, and NH_3^+groups could be assigned to the resonance peaks in ^{1}H NMR spectrum. However, in some of these energetic salts, the number of active hydrogen atoms was found less than the suggested theoretical value. For example, the protons of ammonium cation appeared coupling to ^{14}N as a triplet at 7.08 ppm with coupling constant 51.10 Hz and the number of the protons were about four rather than eight. It might be attributed to the exchange of active hydrogen atoms and was confirmed by deuterium exchange experiments in the ^{1}H NMR spectrum. From the ^{1}H NMR signals of methylamine and pyridine salts (**4i** and **4j**), it was noted that the deprotoned **4** was well combined with two equiv of the amines. The carbon signals in nitrogen-rich cations could be found in ^{13}C NMR spectra. Mass spectrometry and elemental analyses well verified the structure. The measured values of the molecular weight for the energetic salts, 718 or 719, were in excellent accordance with molecular weight of the energetic anion.

Table 1 Physical properties of 3,3'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis (ethene-2,1-diyl))bis(2,4,6-trinitrophenol) (**4**) and its energetic salts (**4a–m**) in comparison to other typical energetic materials

Entry	T_m [a]	T_d [b]	*D* [c]	OB [d]	$\Delta_f H_{Lat}$ [e]	$\Delta_f H$ [f]	IS [g]	P [h]	v_D [i]	*Bri* [j]
3	226	275.1	1.67	-95.0	-	- 69.4	＞40	21.9	6313	84.7
4	210	268.3	1.88	-63.4	-	-129.6	31	26.6	7043	112.2
4a	dec	300.4	1.78	-66.9	936.7	139.1	＞40	28.5	7471	114.2
4b	245	299.8	1.81	-60.1	927.5	234.5	＞40	29.2	7574	119.3
4c	dec	311.3	1.79	-66.4	924.3	438.7	＞40	31.4	7971	121.3
4d	dec	290.7	1.73	-71.6	887.8	264.0	＞40	30.3	7838	123.2
4e	241	272.1	1.69	-71.0	867.2	290.6	＞40	30.8	7981	130.2
4f	206	269.5	1.74	-70.4	865.5	495.5	＞40	33.9	8427	137.3
4g	210	268.4	1.68	-69.9	842.1	723.9	＞40	34.1	8527	144.4
4h	dec	291.7	1.82	-65.8	905.2	356.6	＞40	30.8	7822	121.2
4i	dec	293.2	1.68	-76.8	902.1	350.9	＞40	26.7	7268	103.9
4j	263	288.6	-	-	-	-	-	-	-	-
4k	dec	290.2	-	-	-	-	25	-	-	-
4l	dec	298.1	-	-	-	-	24	-	-	-
4m	dec	295.3	-	-	-	-	15	-	-	-
TNT[3d]	80.4	295	1.65	-74.0	-	-67.0	15	19.5	6881	100
HNS[14]	318	332	1.74	-67.5	-	-67.8	5	20.1	7000	101.6
TATB[5a]	324	324	1.93	-55.8	-	-140	50	31.2	8114	107
HMX	282	287	1.94	-21.6	-	104.8	7.4	39.6	9320	155

[a] Melting point [℃]. [b] Thermal degradation temperature (onset) under nitrogen gas (DSC, 5 ℃ /min) [℃]. [c] Measured density (gas pycnometer, 25 ℃) [g cm^{-3}]. [d] Oxygen balance, the compound with the molecular formula of $C_aH_bN_cO_d$, OB(%) = 1600[(d - 2a- b/2)/ M_w] [%]; Mw = molecular weight. [e] Calculated molar lattice energy [KJ mol^{-1}]. [f] Calculated heat of formation [KJ mol^{-1}]. [g] Impact sensitivity [J]. According to UN recommendations on the transport of dangerous goods: Impact: insensitive ≥ 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J. [h] Calculated detonation pressure [GPa]. [i] Calculated detonation velocity [m s^{-1}]. [j] The calculated brisance relative to TNT [15] (= 100).

Physicochemical Properties: Thermal Stability, Heat of Formation, and Detonation Parameters.

The phase transition temperatures and thermal stability of all the compounds were studied using differential scanning calorimetry (DSC) and digital micro-melting point apparatus (Table 1). All of the synthesized compounds melted more than 200 ℃ and prior to decomposition. Among the **4**-based salts, aminoguanidinium salt 4f showed the lowest melting point (206 ℃), whereas the melting points of hydroxylaminium salt **4b**, diaminoguanidinium salt **4e** as well as pyridinium salt **4j** were higher than 240℃. The decomposition temperatures of all ionic compounds were higher than that of compound **4** in the range from 268.4 ℃ (**4g**) to 311.3 ℃ (**4c**). The hydrazinium salt 4c showed the highest decomposition temperature among the salts (T_d = 311.3 ℃), which was comparable to the benchmark HNS (T_d = 332 ℃) and superior to those of TNT (T_d = 295 ℃) and HMX (T_d = 287 ℃). Decomposition of explosives might be caused by the reactions in or between molecules at a certain temperature. They exhibited excellent thermal stability (**4a-d**, **4h-m** nearly 300 ℃), which most likely could be attributed to the extensive and strong hydrogen-bonding interactions and the conjugated system.

Oxygen balance (OB) was an expression that used to indicate the degree to which an explosive could be oxidized. The sensitivity, strength, and brisance of an explosive are all somewhat dependent upon oxygen balance and tend to approach their maximum values as the oxygen balance approaches zero. Although all of the salts described in this paper had negative OB values, all of them presented better oxygen balance than TNT (-74%) except **4i** (-76.8%). As shown in Table 1, **4b** exhibited the least negative oxygen balance of -60.1%. Densities of the energetic materials were measured with a gas pycnometer, and found in the range of 1.67–1.88 g cm^{-3}, which seemed the densities of salts were lower than that of the parent compounds **4** (1.88 g cm^{-3}). Nevertheless, they were much higher than the density of TNT (1.65 g cm^{-3}) and comparable to HNS (1.74 g cm^{-3}). Among the ionic salts, uronium salt (**4h**) had the highest density at 1.82 g cm^{-3}. The relatively high densities were presumably ascribed to the high symmetry of the anion and the extensive intra- and intermolecular hydrogen bonds in these salts.

Impact sensitivity measurements were made by using standard BAM Fall hammer techniques with 40.0 mg samples. The parameters of impact sensitivity ranged from 15 J to greater than 40 J. Neutral compound **4** had an impact sensitivity of 31 J. Salts **4a-i** were insensitive (>40 J), whereas the metallic salts **4k-m** were sensitive to impact, detonating in a loud noise. In general, all of the nonmetallic energetic salts might be served as candidates for energetic materials.

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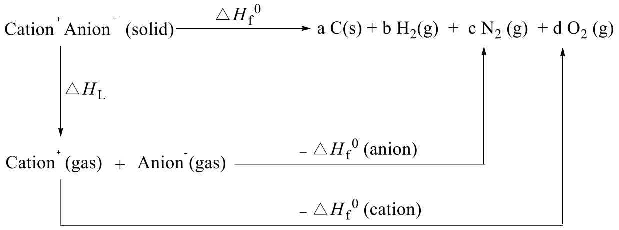
The heat of formation was another important parameter to be considered in the design of energetic salts, obtained by calculations with Gaussian 03 (Revision D.01) suite of programs. Recently, significant progress had been made in the theoretical prediction of thermal properties of energetic salts.[14, 15] The calculated standard enthalpies of formation for the anion of **4** was -177.0 kJ mol^{-1}, which was obtained on the basis of isodesmic reactions and Born–Haber cycles. The triaminoguanidinium salt possessed the highest heats of formation when paired with the anion (**4g**: 723.9 kJ mol^{-1}). Also, the diaminoguanidinium salt **4f** owned a higher heats of formation of 495.5 kJ mol^{-1}. Ammonium salt **4a** possessed large lattice energies, which lead to low positive heats of formation of the salts. As calculated by Zhu et al.[16], it showed that the heat of formation of a cation or anion increases as the number of nitrogen atoms increases and nitrogen-nitrogen bonds usually contribute a lot to positive heat of formation.

The detonation velocity vD [m s^{-1}] and pressure P [GPa] were the most important parameters for evaluating the detonation characteristics of energetic materials. These parameters were directly related to the density and heat of formation. They were obtained by calculation using Kamlet–Jacobs equations [Eqs. (4), (5) and (6), see below]. As shown in Table 1, for the **4**-based salts, the calculated detonation pressures lied in the range of 26.7–34.1 GPa, which were higher than that of TNT (19.5 GPa). The calculated detonation velocities fall in the range of 7268–8527 m s^{-1}, which were better than that of TNT (6881 m s^{-1}) and HNS (7000 m s^{-1}). Thus, the salts could be acted as competitive energetic materials.

The brisance parameter could be directly related to detonation pressure or detonation velocity and indirectly to heat of detonation. It was indicated that the detonation performance of energetic compounds was dependent on their molecular structure. Mohammad Hossein Keshavarz[17] reported a reliable and simple method for the prediction of the brisance through with the general formula $C_aH_bN_cO_d$. As shown in Table 1, the calculated brisance of **4-4i** ranges between 103.9 (**4i**) and 144.4 (**4g**), which were comparable with currently used explosives (TNT: 100, HNS: 101.6, TATB: 107).

Theoretical study: Calculations were performed with the Gaussian 03 (Revision D.01) suite of programs.[18] The geometric optimization of the structures were carried out by using the B3LYP functional with 6-31+ G** basis set, and single energy points were calculated at the MP2/6-311+ + G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.



Scheme 4 Born–Haber cycle for the formation of energetic salts.

For an ionic crystal with formula unit $M_p X_q$, where M denotes the cation and X denotes the anion. The values of heats of formation for the cations are available in the literature.[3d, 5b, 15d] Based on a Born–Haber energy cycle (Scheme 4), the standard heats of formation of a salt can be simplified by the formula given in Equation (1):

$$\triangle H_f^0\ (\text{salt, 298K}) = \triangle H_f^0\ (\text{cation, 298K}) + \triangle H_f^0\ (\text{anion, 298K}) - \triangle H_L \quad (1)$$

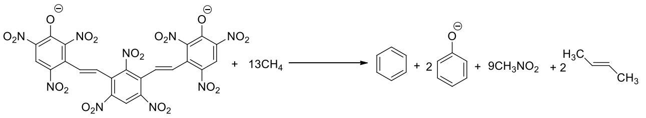
where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al[19]. [Equation (2)]:

$$\triangle H_L = U_{pot} + [p(n_M/2 - 2) + q(n_x/2 - 2)]RT \quad (2)$$

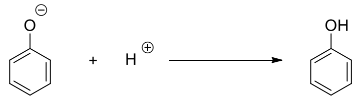
In this equation, n_M and n_X depend on the nature of the ions M^{p+} and X^{q-}, respectively, and are equal to three for monoatomic ions, five for

$$U_{pot}\ [\text{KJ mol}^{-1}] = \gamma\ (\rho_m / M_m)^{1/3} + \delta \quad (3)$$

linear polyatomic ions, and six for nonlinear polyatomic ions. The equation for lattice potential energy U_{pot} [Equation (3)] has the form: where ρ_m [g cm^{-3}] is the density, M_m is the chemical formula mass of the ionic material, and values for the coefficients γ [kJ mol^{-1} cm] and δ [kJ mol^{-1}] are taken from the literature, they are 8375.6 kJ mol^{-1} cm and -178.8 kJ mol^{-1}, respectively.[16, 19-20] The heats of formation of the anion of 4 were computed by using the method of isodesmic reactions and protonation reaction (Scheme 5 and Scheme 6).



Scheme 5 Isodesmic reactions for calculations of heats of formation.



Scheme 6 Protonation reactions for calculations of heats of formation.

The enthalpy of reaction is obtained by combining the MP2/6-311 + + G** energy difference for the reaction, the scaled zero-point energies, and other thermal factors. Thus, the heats of formation of the species being investigated can be readily extracted. With values of the heats of formation and densities, the detonation pressure (P) and velocity (vD) were calculated based on Kamlet–Jacobs equations [Equations (4) and (5)]: [7b, 7c]

$$D = (1.011 + 1.312\rho)(N\bar{M}^{0.5}Q^{0.5})^{0.5} \quad (4)$$

$$P = 1.558\rho^2 N\bar{M}^{0.5}Q^{0.5} \quad (5)$$

For the compounds with the molecular formula of $C_a H_b O_c N_d$, $2a + b/2 > c \geq b/2$ (suitable for all the salts in this study), Q can be calculated according to Equation (6):

$$Q = \frac{28.9\,b + 94.05\left(\frac{c}{2} - \frac{b}{4}\right) + 0.239\triangle H_f^0}{M} \times 10^3 \quad (6)$$

where P is the detonation pressure (GPa), D is the detonation velocity (km/s), ρ is the packed density (g/cm^3), The measured density was used for the calculation here. N is the moles of gas produced per gram of explosives, $\bar{M}$ is the average molar weight of detonation products, and Q is the chemical energy of detonation (kJ/g). N, $\bar{M}$, and Q are decided according to the largest exothermic principle; i.e., for the explosives with C H N O elements, all of the N atom converts into N_2, the O atom forms H_2O with the H atom first, and the remainder forms CO_2 with the C atom.

Also, the brisance parameters of pure energetic compounds were based on the elemental composition. For the $C_aH_bN_cO_d$ energetic compounds, the predicted data could be specified according to the following Equation (7):

$$\text{Bris}_{\text{relTNT}} = 85.5 + 4.812c + 2.556(\ d\text{-}a\text{-}b/2\ ) \qquad (7)$$

where Bris $_{\text{relTNT}}$ is the relative brisance with respect to TNT.

Conclusions

In this work, we reported an efficient two–step nitration for the syntheses of 4,4'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(1,3-dinitrobenzene) (**3**) as well as 3,3'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(2,4,6-trinitrophenol) (**4**) and its nitrogen-rich salts(**4a-m**), leading to thermally stable energetic materials. Both the neutral compound and its salts exhibit good thermal stability (T_d = 268.4–311.3 ℃) and energetic properties (detonation velocity 7268–8527 m s^{-1}, detonation pressure 26.7–34.1 GPa, brisance parameters 103.9–144.4) that exceed those of conventional TNT. In addition, most of these compounds show higher density in the range of 1.67–1.88 g cm^{-3} than TNT and are comparable with HNS. Also, they were characterized with respect to impact sensitivity, which exhibit low impact sensitivities (> 40 J). The good property parameters meet the requirement of high temperature explosives.

Experimental Section

Safety Precautions

Although none of the compounds described herein have exploded or detonated in the course of this research, these materials should be handled with extreme care using the best safety practices.

General Methods

All chemical reagents and solvents (analytical grade) were used as supplied unless otherwise stated. All experiments were monitored by thin-layer chromatography (TLC), TLC plates were visualized by exposure to ultraviolet light (254 nm). ^1H and ^{13}C spectra were recorded on a Bruker Avance III 500 MHz Digital NMR Spectrometer, using $CDCl_3$ or DMSO-d_6 as a solvent and the chemical shifts were reported in δ (ppm) values. Coupling constants were reported in hertz (Hz). Mass spectra were obtained using an electrospray (ESI-TOF) mass spectrometer 6500 Series and a Bruker Daltonics flexAnalysis instrument. Infrared spectra were recorded using Bruker Tensor 27 with the sample dispersed in a KBr pellet and were reported in terms of frequency of absorption (cm^{-1}). The melting points were determined on digital micro-melting point apparatus. The decomposition points were recorded using differential scanning calorimeter (DSC). The following procedures were used in experiments for each sample: cooling from 50 ℃ and heating to 450 ℃ at 5 ℃ min^{-1}. Densities were measured at room temperature using gas pycnometer. Elemental analyses were performed on a CE-440 Elemental Analyzer. Impact sensitivity (IS) was measured through using 10 kg mass dropped from 40 cm. Detonation pressures (*P*) and detonation velocities (*D*) were calculated according to the Kamlet–Jacobs equations.

Syntheses

2,4,6-trinitro-m-xylene [21] *m*-Xylene (10.62 g, 0.10 mol) was added slowly to a mixture of concentrated sulfuric acid (50.0 mL) and fuming nitric acid (20.0 mL) below 20 ℃. The mixture was heated at 80 ℃ for 1 h and then elevated to 110 ℃ for 4 h. After cooling down to room temperature the mixture was poured in to crashed ice (800.00 g). The precipitate was filtered and crystallized using 100.0 mL 2-butanone to give a pure product as a white solid (19.30 g, 80%).

((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))dibenzene **(1)** Prepared according to the literature method.[9] Yellow solid, m. p. 149-150 ℃, (lit. 149.5-151.1 °C), IR (ν, cm^{-1}): 3095, 1634, 1588, 1541, 1451, 1395, 1344, 968. ^1H NMR (500MHz, $CDCl_3$), δ 8.72 (s, 1H), 7.50-7.37 (m, 10H), 7.20 (d, *J* = 16.60Hz, 2H), 6.90 (d, *J* =16.60Hz, 2H).

2,2'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1 diyl))bis(nitro-benzene) **(2)** To acetic anhydride (15.0 mL), initially at room temperature, was added 68 % nitric acid (1.86 g, 20.0 mmol) over a period of approximately 25 min, maintaining the temperature about 25 ℃. The nitration solution was then cooled to 10 ℃ and 2 drops of concentrated sulfuric acid was added as catalyst. Following the addition of compound 1 (0.84 g, 2.0 mmol) in small portions, the reaction mixture with rapid stirring at 30 ℃. The solid was dissolved first and then a green solid was formed after 5 min. The reaction mixture then poured into 150.0 mL of water. Finally, after hydrolysis of the acetic anhydride was complete, the product was collected by filtration.

Green yellow solid (0.87 g, 86%), recrystallization from acetone, m. p. 212-213 ℃, IR (ν, cm^{-1}): 3097, 1629, 1603, 1550, 1524, 1341, 975; ^1H NMR (500MHz, DMSO-d_6), δ 9.07 (s, 1H）8.09 (d, *J* =8.15Hz, 2H), 7.86 (d, *J*=3.95Hz, 2H), 7.69-7.66 (m, 4H), 7.50 (d, *J* =16.45Hz, 2H), 7.21 (d, *J* =16.45Hz, 2H); ^{13}C NMR (126MHz, DMSO-d_6), δ 149.77, 147.23, 146.48, 133.59, 131.04, 129.89, 129.54, 128.33, 127.86, 124.23, 122.43, 121.96. HRMS calc. for $C_{22}H_{13}N_5O_{10}$ $(M+H)^+$: 508.0210, found (M+H) 508.0206, (M+ Na) 530.0121, (M+ K） 545.9988.

4,4'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(1,3-dinitrobenzene) **(3)** Fuming nitric acid (1.33 g, 20.0 mmol) was added slowly by funnel to a concentrated sulfuric acid (20.0 mL) solution of compound 2 (1.01 g, 2.0 mmol）below 10℃. The mixture was kept at room temperature, and gave a red-brown solution. The reaction was quenched by pouring into 150.00 g of crashed ice, and pale yellow solid was formed. The solid was collected by filtration and crystallized by acetone to give a pure product.

Pale yellow solid (0.57 g, 48%), m. p.226-227 ℃, IR (ν , cm^{-1}): 3098, 1625, 1608, 1555, 1530, 1342, 970; ^1H NMR (500MHz, DMSO-d_6), δ 9.10 (s, 1H), 8.79 (d, *J* =2.30Hz, 2H), 8.66-8.64 (dd, J_1 =2.30Hz, J_2 =8.65Hz, 2H), 8.11 (d, *J* =8.65Hz, 2H), 7.73 (d, *J* =16.45Hz, 2H), 7.26 (d, *J* =16.45Hz, 2H); ^{13}C NMR (126MHz, DMSO-d_6), δ 149.57, 147.00, 146.82, 146.71, 135.27, 129.95, 129.58, 129.38, 127.63, 125.33, 122.61, 119.80. HRMS calc. for $C_{22}H_{11}N_7O_{14}$ $(M+H)^+$: 597.0364, found (M+H) 597.0349, elemental analysis, calcd (%) for $C_{22}H_{11}N_7O_{14}$: C: 44.23; H: 1.86; N: 16.41; Found, C: 44.18; H: 1.82; N: 16.33.

3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))diphenol. To a mixture of 2,4,6-trinitro-m-xylene (1.21 g, 5.0 mmol), 3-hydroxybenzaldehyde (1.22 g, 10.0 mmol), and mixed solvents of benzene (30.0 mL) and dioxane (25.0 mL) in a 100 mL round-bottomed flask was added piperidine (1.0 mL) in portions and the resulting mixture was heated to reflux using a condenser connected through a Dean-Stark trap. The reaction mixture was a homogeneous solution at reflux temperature, initially a light orange color which gradually deepened to dark brown during the heating period. After 10 h at reflux, heating was discontinued and the solvents

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were collected to give the crude product. The bright yellow solid was isolated via silica gel column chromatography (Hexane/ Ethyl acetate= 5/1).

Bright yellow solid (2.04 g, 91%), m. p. 194-196 °C, IR (ν , cm^{-1}): 3400, 3095, 1635, 1609, 1586, 1514, 1395, 1323, 972; ^1H NMR (500MHz, DMSO-d_6), δ 9.60 (s, 2H), 9.00 (s, 1H), 7.29 (d, *J* = 16.60Hz, 2H), 7.23 (t, *J* = 7.85Hz, 2H), 6.98 (d, *J* = 7.70Hz, 2H), 6.94 (s, 2H), 6.81-6.78（dd, J_1 =8.10Hz, J_2 =1.75Hz, 2H), 6.78 (d, *J* =16.60Hz, 2H). ^{13}C NMR (126MHz, DMSO-d_6), δ 157.26, 149.90, 145.98, 136.58, 135.74, 129.96, 129.49, 122.13, 117.87, 116.63, 116.31, 112.99. HRMS calc. for $C_{22}H_{15}N_3O_8$ $(M+H)^+$: 450.0968, found 450.0975, 511.0722(M+Na+K).

***3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(2,4,6-trinitrophenol)* (4)** The addition of 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1- diyl))diphenol (2.25 g, 5.0 mmol) to 96% sulfuric acid (10.0 mL) produced a dark green colored slurry. This slurry was chilled in an ice and water bath and 30% oleum was added (15 mL) slowly with stirring, keeping the temperature of the mixture under 30 ℃. The resulting dark brown solution was allowed to stand at room temperature for 15 min, then heated to 90 ℃ on the steam bath and held at that temperature for 2 h. After cooling to room temperature this solution was added slowly, with rapid stirring, during 30 min., to a mixture of 68% nitric acid (8.0 mL) and 96% sulfuric acid (8.0 mL) at room temperature and then heated to 50 ℃ for 1 h. Initially the reaction mixture was a black-brown solution, but after about 10 min the color of the mixture turned to red accompanied by some foams. The mixture was then drowned in crashed ice and water (300 mL). The product was filtered, washed with water, and dried.

Light yellow solid (1.51 g, 42%)，crystallized from methanol/water, m. p. 209-210 °C, IR (ν, cm^{-1}): 3422, 3212, 3107, 2908, 1630, 1595, 1553, 1451, 1343, 1167, 966, 923, 825, 778, 754, 701. ^1H NMR (500MHz, DMSO-d_6), δ 8.96 (s, 1H), 8.74 (s, 2H), 8.27 (br, 2H), 7.06 (d, *J* =16.75Hz, 2H), 6.74 (d, *J* =16.75Hz, 2H). ^{13}C NMR (126MHz, DMSO-d_6), δ 159.35, 149.07, 147.10, 146.95, 135.99, 130.42, 127.74, 127.69, 125.50, 123.81, 121.88, 120.43. HRMS calc. for $C_{22}H_9N_9O_{20}$ (M):718.9174, found 718.9176, elemental analysis, calcd (%) for $C_{22}H_9N_9O_{20}$: C: 36.73; H: 1.26; N: 17.52; Found, C: 36.61; H: 1.14; N: 17.44.

General procedures for the preparation of 3,3'-((1*E*,1'*E*)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(2,4,6-trinitrophenol) based salts (4a–m):

The **4** (0.72 g, 1.0 mmol) was dissolved in methanol (13.0 mL) followed by adding a solution of 2 equiv ammonium chloride, hydroxylamine hydrochloride, hydrazine monohydrochloride, guanidine hydrochloride, aminoguanidine hydrochloride, diaminoguanidine monohydrochloride, triaminoguanidine monohydrochloride, urea, methylamine, pyridine, potassium nitrate, silver nitrate or 0.5 equiv copper nitrate (50 wt% in water), respectively. After stirring at room temperature for 1 h, the yellow precipitate was filtered off and dried in an oven at 70 ℃ for 4 h.

***Diammonium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis (2,4,6 –trinitrophenolate.* (4a)** Yellow needle-shaped crystal (0.65 g, 86%), IR (ν , cm^{-1}): 3423, 3175, 3087, 1604, 1520, 1451, 1406, 1340, 1304, 1257, 1153, 1066, 955, 924, 825, 788, 752, 712, 687. ^1H NMR (500MHz, DMSO-d_6), δ 8.94 (s, 1H), 8.73 (s, 2H), 7.08 (t, *J* =51.10Hz, 4H), 7.04 (d, *J* =16.75Hz, 2H), 6.72 (d, *J* =16.75Hz, 2H). ^{13}C NMR (126MHz, DMSO-d_6), δ 159.37, 149.07, 147.10, 146.94, 135.97, 130.39, 127.76, 127.72, 125.52, 123.85, 121.91, 120.47. Hydrogen/deuterium exchange experiments, ^1H NMR (500 MHz, D_2O-DMSO-d_6), δ 8.92 (s, 1H), 8.72 (s, 2H), 7.03 (d, *J* =16.75Hz, 2H), 6.71 (d, *J* =16.75Hz, 2H). MS (FAB^-): 717.8, elemental analysis, calcd (%) for $C_{22}H_{15}N_{11}O_{20}$: C: 35.07; H: 2.01; N: 20.45; Found, C: 35.00; H: 1.98; N: 19.59.

***Dihydroxylammonium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl)) bis(2,4,6-trinitrophenolate)* (4b)** Yellow solid (0.70 g, 89%), m.p. 245 °C, IR (ν , cm^{-1}): 3424, 3203, 3096, 1604, 1542, 1451, 1341, 1308, 1262, 1157, 1071, 1005, 964, 910, 825, 788, 755, 707. ^1H NMR (500MHz, DMSO-d_6), δ 10.08 (s, 3H), 8.95 (s, 1H), 8.74 (s, 2H), 7.09 (t, *J* = 51.15Hz, 1H), 7.06 (d, *J* = 16.80Hz, 2H), 6.74 (d, *J* = 16.80Hz, 2H). ^{13}C NMR (126MHz, DMSO-d_6), δ 159.35, 149.07, 147.10, 146.95, 135.99, 130.42, 127.74, 127.69, 125.50, 123.81, 121.88, 120.43. MS (FAB^-): 718.0, elemental analysis, calcd (%) for $C_{22}H_{15}N_{11}O_{22}$: C: 33.64; H: 1.92; N: 19.62; Found, C: 33.48; H: 1.88; N: 19.56.

***Dihydrazinium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis (2,4,6-trinitrophenolate)* (4c)** Yellow solid (0.72 g, 92%), IR (ν , cm^{-1}): 3369, 3224, 3105, 1626, 1596, 1547, 1452, 1343, 1263, 1165, 1067, 964, 924, 826, 781, 754, 703. ^1H NMR (500MHz, DMSO-d_6), δ 8.96 (s, 1H), 8.75 (s, 2H), 7.43 (s, 6H), 7.06 (d, *J* = 16.75Hz, 2H), 6.74 (d, *J* = 16.75Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6), δ 159.16, 149.07, 147.01, 146.95, 136.00, 130.36, 127.78, 127.69, 125.47, 124.06, 121.89, 120.51. MS (FAB^-): 717.9, elemental analysis, calcd (%) for $C_{22}H_{17}N_{13}O_{20}$: C: 33.73; H: 2.19; N: 23.24; Found, C: 33.68; H: 2.21; N: 23.16.

***Diguanidinium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis (2,4,6-trinitrophenolate)* (4d)** Bright yellow solid (0.75 g, 90%), IR (ν , cm^{-1}): 3463, 3419, 3362, 3198, 3091, 1650, 1604, 1535, 1482, 1452, 1337, 1302, 1251, 1155, 1065, 958, 927, 907, 825, 790, 755, 717. ^1H NMR (500MHz, DMSO-d_6), δ 8.94 (s, 1H), 8.73 (s, 2H), 7.04 (d, *J* = 16.80Hz, 2H), 6.89 (s, 12H), 6.72 (d, *J* = 16.80Hz, 2H). ^{13}C NMR (126MHz, DMSO-d_6), δ 159.38, 158.24, 149.08, 147.11, 146.95, 135.99, 130.42, 127.77, 127.71, 125.52, 123.87, 121.89, 120.46. MS (FAB^+):59.3 ($CN_3H_6^+$); (FAB^-): 717.8, 718.9, elemental analysis, calcd (%) for $C_{24}H_{19}N_{15}O_{20}$: C: 34.42; H: 2.29; N: 25.09; Found, C: 34.38; H: 2.22; N: 24.89.

***Diaminoguanidinium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1- diyl))bis(2,4,6-trinitrophenolate)* (4e)** Yellow solid (0.75 g, 86%), m.p. 241 ℃, IR (ν , cm^{-1}): 3439, 3361, 3095, 1669, 1601, 1543, 1453, 1338, 1301, 1257, 1155, 1070, 959, 926, 907, 825, 789, 754, 708. ^1H NMR (500MHz, DMSO-d_6), δ 8.94 (s, 1H), 8.73 (s, 2H), 8.53(s, 2H), 7.23(br, 8H), 7.05 (d, *J* = 16.75Hz, 2H), 6.73 (d, *J* = 16.75Hz, 2H), 4.66(s, 4H). ^{13}C NMR (126 MHz, DMSO-d_6), δ 159.37, 157.36, 149.07, 147.11, 146.95, 135.99, 130.42, 127.77, 127.70, 125.51, 123.86, 121.88, 120.45. MS (FAB^-): 718.0, 719.0, elemental analysis, calcd (%) for $C_{24}H_{21}N_{17}O_{20}$: C: 33.23; H: 2.44; N: 27.45; Found, C: 33.33; H: 2.42; N: 27.49.

***Di(diaminoguanidinium) 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1- diyl))bis(2,4,6-trinitrophenolate)* (4f)** Yellow solid (0.76 g, 85%), m. p. 206 °C, IR (ν , cm^{-1}): 3441, 3315, 3236, 1681, 1604, 1539, 1454, 1395, 1338, 1302, 1258, 1154, 1069, 997, 958, 927, 828, 787, 754, 704. ^1H NMR (500MHz, DMSO-d_6), δ 8.96(s, 1H), 8.75 (s, 2H), 8.55(s, 4H), 7.14(s, 4H), 7.07 (d, *J* =16.75Hz, 2H), 6.74 (d, *J* =16.75Hz, 2H), 4.36(s, 8H). ^{13}C NMR (126MHz, DMSO-d_6), δ 159.37, 159.20, 149.08, 147.11, 146.95, 136.00, 130.43, 127.76, 127.71, 125.52, 123.83, 121.89, 120.44. MS (FAB^-): 740.0

(M+Na), elemental analysis, calcd (%) for $C_{24}H_{23}N_{19}O_{20}$: C: 32.12; H: 2.58; N: 29.65; Found, C: 32.03; H: 2.46; N: 28.99.

***Ditriaminoguanidinium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1- diyl))bis(2,4,6-trinitrophenolate)* (4g)** Yellow solid (0.77 g, 83%), m. p. 210 °C, IR (ν , cm^{-1}): 3425, 3344, 3110, 2997, 1628, 1548, 1454, 1338, 1300, 1260, 1154, 1102, 1072, 1046, 956, 912, 827, 788, 752, 683. ^{1}H NMR (500MHz, DMSO-d$_6$), δ 10.19 (s, 6H), 8.95 (s, 1H), 8.74 (s, 2H), 7.06 (d, J =16.75Hz, 2H), 6.73 (d, J =16.75Hz, 2H). ^{13}C NMR (126MHz, DMSO-d$_6$), δ 159.37, 159.20, 149.08, 147.11, 146.95, 136.00, 130.43, 127.76, 127.71, 125.52, 123.83, 121.89, 120.44. MS (FAB$^-$): 717.9, 718.9; elemental analysis, calcd (%) for $C_{24}H_{25}N_{21}O_{20}$: C: 32.08; H: 2.72; N: 31.71; Found, C: 32.04; H: 2.66; N: 31.86.

***Diuronium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis(2,4,6- trinitrophenolate)* (4h)** Yellow solid (0.67 g, 80%), IR (ν , cm^{-1}): 3475, 3176, 3090, 1706, 1600, 1542, 1452, 1403, 1341, 1306, 1258, 1155, 1066, 960, 924, 825, 783, 753, 712. ^{1}H NMR (500MHz, DMSO-d$_6$), δ 8.96 (s, 1H), 8.75 (s, 2H), 7.10 (t, J = 51.15Hz, 2H), 7.06 (d, J = 16.80Hz, 2H), 6.74 (d, J = 16.80Hz, 2H), 5.35 (br, 8H). ^{13}C NMR (126MHz, DMSO-d$_6$), δ 160.36, 159.25, 149.08, 147.05, 146.95, 136.00, 130.38, 127.78, 127.69, 125.48, 124.00, 121.89, 120.49. MS (FAB$^+$):61.2 ($CH_5N_2O^+$), (FAB$^-$): 718.0, 719.0; elemental analysis, calcd (%) for $C_{24}H_{17}N_{13}O_{22}$: C: 34.34; H: 2.04; N: 21.69; Found, C: 34.22; H: 2.00; N: 21.76.

***Dimethanaminium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl)) bis(2,4,6-trinitrophenolate)* (4i)** Bright yellow solid (0.67 g, 86%), IR (ν , cm^{-1}): 3426, 3258, 3080, 1603, 1543, 1470, 1336, 1303, 1259, 1156, 1070, 960, 932, 826, 790, 753, 707. ^{1}H NMR (500MHz, DMSO-d$_6$), δ 8.94 (s, 1H), 8.73 (s, 2H), 7.49 (s, 6H), 7.04 (d, J = 16.75Hz, 2H), 6.72 (d, J = 16.75Hz, 2H), 2.36 (s, 6H).^{13}C NMR (126MHz, DMSO-d$_6$), δ 159.40, 149.08, 147.10, 146.95, 135.97, 130.40, 127.78, 127.71, 125.52, 123.94, 121.90, 120.48. MS (FAB$^-$): 718.0; elemental analysis, calcd (%) for $C_{24}H_{19}N_{11}O_{20}$: C: 36.89; H: 2.45; N: 19.72; Found, C: 36.82; H: 2.34; N: 19.66.

***Dipyridinium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis (2,4,6-trinitrophenolate)* (4j)** Yellow solid (0.80 g, 91%), m. p. 263°C, IR (ν, cm^{-1}): 3424, 3242, 3096, 2750, 1597, 1538, 1486, 1455, 1307, 1265, 1156, 1069, 963, 925, 786, 755, 708. ^{1}H NMR (500MHz, DMSO-d$_6$), δ 8.95 (s, 1H), 8.93 (d, 5.20Hz, 5H), 8.61-8.58 (tt, J_1 = 7.85Hz, J_2 = 1.45Hz, 2H), 8.73 (s, 2H), 8.08-8.05 (dd, J_1 = 6.7Hz, J_2 = 0.95Hz, 5H), 7.05 (d, J = 16.75Hz, 2H), 6.73 (d, J = 16.75Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d$_6$), δ 159.37, 149.07, 147.10, 146.95, 145.58, 141.85, 135.99, 130.42, 127.77, 127.71, 126.61, 125.52, 123.86, 121.91, 120.46. MS (FAB$^-$): 718.0, 719.0; elemental analysis, calcd (%) for $C_{32}H_{19}N_{11}O_{20}$: C: 43.80; H: 2.18; N: 17.56; Found, C: 43.82; H: 2.22; N: 17.51.

***Potassium 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis (2,4,6-trinitrophenolate)* (4k)** Yellow solid (0.64 g, 80%), IR (ν, cm^{-1}): 3413, 2073, 2021, 1659, 1532, 1461, 1354, 1248, 1122, 1086, 961, 930, 776, 757, 716. MS (FAB$^-$): 718.

***Silver 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis (2,4,6-trinitrophenolate)* (4l)** Yellow solid (0.77 g, 82%), IR (ν , cm^{-1}): 3445, 2081, 2011, 1602, 1544, 1452, 1343, 1256, 1112, 1056, 962, 927, 788, 755, 706. MS (FAB$^-$): 717.9.

***Copper 3,3'-((1E,1'E)-(2,4,6-trinitro-1,3-phenylene)bis(ethene-2,1-diyl))bis (2,4,6-trinitrophenolate)* (4m)** Green yellow solid (0.66 g, 85%), IR (ν, cm^{-1}): 3644, 3615, 3569, 3419, 3203, 3117, 1608, 1574, 1543, 1480, 1451, 1342, 1269, 1161, 1078, 964, 927, 782, 758, 714. MS (FAB$^+$): 64.3.

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Notes and references

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Electronic Supplementary Information (ESI) available: NMR and MS Spectra of related compounds. See DOI: 10.1039/b000000x/

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