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Solar-energy-derived strained hydrocarbon as energetic hypergolic fuel

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Experimental Section

Materials: Norbornadiene (97%), 4,4'-Bis(diethylamino)benzophenone (photosensitizer, 99%), oleic acid (99%), trioctylphosphine oxide (TOPO, 99%) were purchased from J&K Scientific Ltd. Ethanol and toluene was reagent grade and purchased from Tianjin Guangfu Fine Chemical Research Institute. Boron (B NPs, 30 nm, 99%) and carbon nanoparticles (C NPs, 35 nm, 99%) were purchased from Beijing Jiaanheng Technology Company and Beijing Kedao Company, respectively. All the reagents were used as received.

Surface-modification of boron and carbon NPs: 0.5 g boron (B) and carbon (C) NPs was added into 10 mL toluene with pre-dispersed TOPO (0.5 g), then the suspension was ultrasonicated for 2 h at *ca.* 40°C. The particles were recovered by centrifugation, and dried at 80°C for 24 h. Then the 0.25 wt% surface-modified B or C were added in the QC, and the solution were stirred and ultrasonically treated for 1 h to make the NPs well suspended in QC.

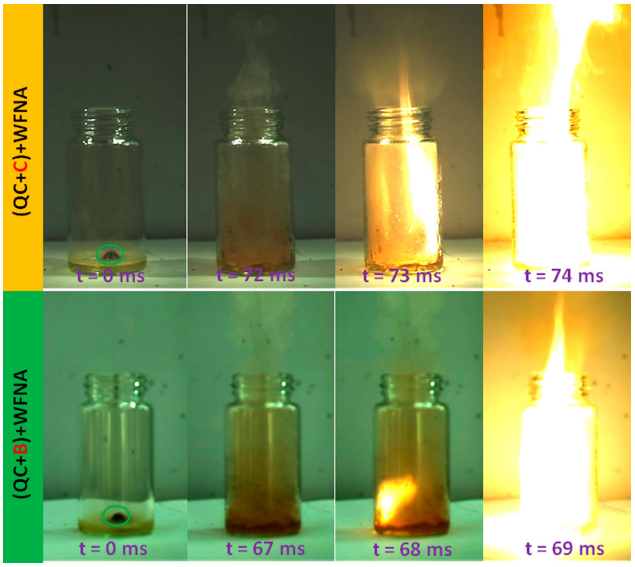

Fig. S1 Ignition process of QC suspension with *WFNA* recorded by high-speed camera. The fuel droplets are marked by green circles.

Computational section in Table 2

1. Calculation method

The heat of formation values of UDMH and EN in our work are directly known from experimental investigations.[1-2] The heat of formation value of QC [$\Delta_f H_m$°(QC)] can be calculated *via* the heat of formation of NBD [$\Delta_f H_m$°(NBD)] and the heat of their isomerization reaction [$\Delta_r H_m$°(isomerization)] (formula (1)). Their isomerization heat can be further calculated by formula (2):

$$\Delta_f H_m^\circ(QC) = \Delta_f H_m^\circ(NBD) + \Delta_r H_m^\circ(isomerization) \quad (1)$$

$$\Delta_r H_m^\circ(isomerization) = H_m^\circ(QC) - H_m^\circ(NBD) \quad (2)$$

where, $\Delta_f H_m^\circ$(NBD) is from the Kumar's experiments[1]; H_m°(QC) and H_m°(NBD) are accurately predicted by Gaussian 09 software package at G4 method level.[3]

Heat of combustion per kilogram of combustible (h) is calculated with formula (3):

$$h = \Delta_c H_m^\circ / M \quad (3)$$

where M is the molar mass of fuel molecules. The standard molar enthalpy of combustion ($\Delta_c H_m^\circ$) is computed based on their combustion reactions with N_2O_4:

$$C_n H_m N_k + (\frac{n}{2} + \frac{m}{8}) N_2O_4(g) = nCO_2(g) + \frac{m}{2} H_2O(g) + (\frac{n}{2} + \frac{m}{8} + \frac{k}{2}) N_2(g)$$

$\Delta_f H_m^\circ$ of $CO_{2(g)}$= −393.51 kJ/mol; $\Delta_f H_m^\circ$ of $H_2O_{(g)}$ = −241.83 kJ/mol; $\Delta_f H_m^\circ$ of $N_2O_{4(g)}$= 11.1 kJ/mol.

Specific impulses (I_{sp}) of the propellants (with N_2O_4) are calculated according to the method of Potapov[4]. Firstly, the heat of combustion per kilogram of combustible (h) is calculated with the above method. To convert h to the specific heat of combustion (H) of a fuel with stoichiometric ratio of combustible to N_2O_4, we derivated the following formula (4) according to the combustion reaction:

$$H = h(12 + x + 14y) / (58 + 12.5x + 14y) \quad (4)$$

where $x=m/n$, $y=k/n$ is respectively the H/C atomic ratio, N/C atomic ratio in the given fuel $C_nH_mN_k$.

Lastly, I_{sp} is given by formula (5):

$$I_{sp} = (2\eta H)^{1/2} / g \quad (5)$$

where the efficiency factor η is taken equal to 0.556 to bring the calculated and experimental specific impulses of dicyclobutylto coincidence.[4]

Density (ρ) of propellant, which is composed of one fuel and its stoichiometric amounts of N_2O_4, is calculated with the following formula (6):

$$\rho_p = \rho_f \rho_{N2O4_{(l)}} (8 + m + 4n) / \left[(m + 4n)\rho_f + 8\rho_{N2O4_{(l)}} \right] \quad (6)$$

Where, the ρ_f is the density of fuel that can be obtained from the database of chemical physical property; $\rho_{N2O4(l)}$=1.443 g/cm^3.

Volumetric Specific Impulsion (I_v) are calculated with:

$$I_v = I_{sp} \times \rho_p \quad (7)$$

2. Enthalpy values

Table S1. Absolute enthalpy values ($H_m°$) of QC and NBD, calculated by Gaussian 09 software.

Species	$H_m°$ [$a.u.$]
NBD	−271.298883
QC	−271.262760

3. Cartesian coordinates of species involved in the predications of isomerization heat between QC and NBD

QC:

C	0.77509500	-0.71023600	-0.75744700
C	-0.77499200	-0.71017700	-0.75758600
C	1.15091300	0.55043600	-0.00002500
C	0.77497400	-0.70997800	0.75778300
C	-0.77510500	-0.71001000	0.75764200
C	-1.15090300	0.55045600	-0.00013800
C	0.00001500	1.53955200	-0.00020800
H	1.42520200	-1.22793600	-1.44898600
H	-1.42503500	-1.22779200	-1.44925000
H	2.18470300	0.87555100	0.00000600
H	1.42503400	-1.22739000	1.44958200
H	-1.42524200	-1.22748200	1.44932400
H	-2.18468400	0.87560100	-0.00024700
H	0.00006100	2.17949400	-0.89006800
H	-0.00002100	2.17969500	0.88951200

NBD:

C	-1.24410900	0.66627500	-0.52082000
C	-1.24410300	-0.66628300	-0.52082300
C	-0.00000400	1.12173500	0.27171700
C	1.24410300	0.66628300	-0.52082100
C	1.24411000	-0.66627500	-0.52081800
C	0.00000400	-1.12173600	0.27171600
C	-0.00000100	-0.00000100	1.35481300
H	-1.93376000	1.33711400	-1.01523200
H	-1.93374800	-1.33712500	-1.01523800
H	-0.00000700	2.15779300	0.60936800
H	1.93374900	1.33712600	-1.01523400
H	1.93376200	-1.33711300	-1.01522900
H	0.00000600	-2.15779400	0.60936600
H	-0.89993800	-0.00000400	1.97620100
H	0.89993400	0.00000200	1.97620300

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