A Strategy Enlightened from the Observed Energetic-energetic Cocrystals of BTF: Cocrystallizing and Stabilizing Energetic Hydrogen-free Molecules with Hydrogenous Energetic Coformer Molecules

Xianfeng Wei, Yu Ma, Xinping Long, and Chaoyang Zhang*

Research Center of Energetic Materials Genome Science, Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), P. O. Box 919-327, Mianyang, Sichuan 621900, China.

Electronic Supporting Information (ESI)

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S1. Crystallographic information of BTF and seven BTF-based Cocrystals discussed.

Table s1. Crystallographic information of crystals discussed.

Explosives	BTF[1]	BTF/CL-20[2]	BTF/DNB[3]	BTF/MATNB[4]
Refcode	BZOFOX	PEHSUS	-	GEXMON
Formula	$C_6N_6O_6$	$C_{12}H_9N_{18}O_{18}$	$C_{12}H_4N_8O_{10}$	$C_{13}H_6N_{10}O_{12}$
Symmetry	Orthorhombic	Orthorhombic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a(Å)	6.923(1)	9.275(5)	9.362	9.332(<1)
b(Å)	19.516(1)	11.946(7)	13.005	12.604(<1)
c(Å)	6.518(1)	21.577(12)	14.911	15.476(<1)
α(°)	90.00	90.00	90.00	90.00
β(°)	90.00	90.00	96.07	90.62(<1)
γ(°)	90.00	90.00	90.00	90.00
V(Å^3)	880.642	2390.713	1609.14	1820.169
Z	4	4	4	4
Density(g/cm^3)	1.901	1.926	1.735	1.804
Temperature (K)	RT	RT	RT	145
Ratio		1:1	1:1	1:1
Explosives	BTF/TNA[4]	BTF/TNAZ[4]	BTF/TNB[4]	BTF/TNT[4]
Refcode	GEXMIH	ZEVNUL	GEXMED	GEXMAZ
Formula	$C_{12}H_4N_{10}O_{12}$	$C_9H_4N_{10}O_{12}$	$C_{12}H_3N_9O_{12}$	$C_{13}H_5N_9O_{12}$
Symmetry	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Space group	monoclinic	triclinic	monoclinic	triclinic
a(Å)	9.402(<1)	6.747(<1)	9.549(<1)	9.338(<1)
b(Å)	12.675(<1)	10.389(<1)	12.567(<1)	12.896(<1)
c(Å)	14.327(<1)	12.348(1)	14.454(<1)	14.729(<1)
α(°)	90.00	70.75(<1)	90.00	88.51(<1)
β(°)	97.41(<1)	88.77(<1)	99.53(<1)	84.16(<1)
γ(°)	90.00	80.12(<1)	90.00	88.94(<1)
V(Å^3)	1693.105	804.394	1710.617	1763.537
Z	4	2	4	4
Density(g/cm^3)	1.884	1.834	1.806	1.805
Temperature (K)	135	RT	RT	145
Ratio	1:1	1:1	1:1	1:1

S2. HBs in seven BTF-based EECCs and seven pure coformer crystals.

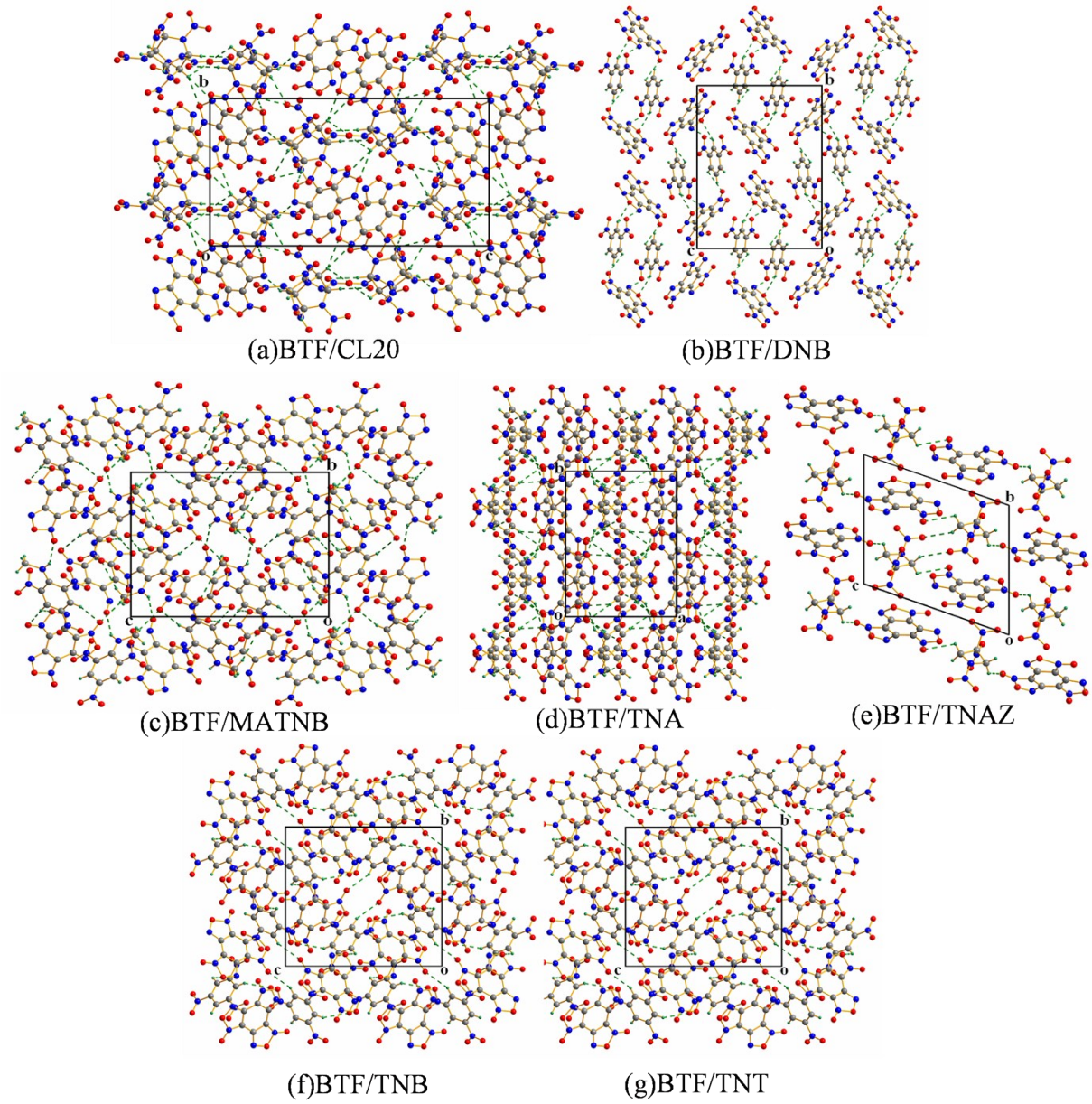

Fig. s1 HBs in the BTF-based EECCs represented by green dash.

Table s2. Geometry and QTAIM analyses of the intermolecular HBs in the BTF-based EECCs.

Explosive	Number	D-H, Å	H···A, Å	A···D, Å	A-H···D,°	ρ, e/Å^3	E_{HB}, kJ/mol
BTF/CL-20	a	0.980	2.706	3.595	150.9	0.00540	4.0
	b	0.980	2.766	3.596	142.9	0.00413	3.5
	c	0.980	2.448	3.338	150.7	0.00983	6.8
BTF/DNB	d	0.929	2.468	3.322	152.8	0.00794	6.5
	e	0.930	2.765	3.352	122.0	0.00475	4.0
BTF/MATNB	f	0.881	2.288	3.066	147.3	0.00912	8.3
	g	0.950	2.626	3.525	158.1	0.00570	4.5
	h	0.980	2.555	3.364	139.9	0.00600	5.1
	i	0.950	2.507	3.454	173.9	0.00745	5.8
BTF/TNA	j	0.949	2.782	3.393	122.9	0.00471	4.0
	k	0.949	2.669	3.610	171.4	0.00536	4.1
	l	0.950	2.759	3.684	164.8	0.00433	3.5
	m	0.880	2.440	2.977	119.8	0.00868	7.8
	n	0.880	2.406	3.186	147.9	0.00750	6.5
BTF/TNAZ	o	0.970	2.795	3.405	121.6	0.00444	3.8
	p	0.970	2.795	3.405	121.6	0.00444	3.8
BTF/TNB	q	0.930	2.759	3.397	126.7	0.00487	4.0
	r	0.930	2.743	3.605	154.6	0.00380	3.1
BTF/TNT1	s	0.981	2.569	3.280	129.4	0.00702	5.8
	t	0.950	2.789	3.718	165.9	0.00400	3.2
	u	0.950	2.714	3.375	127.3	0.00533	4.4
BTF/TNT2	v	0.981	2.588	3.402	140.5	0.00790	5.7
	w	0.980	2.568	3.334	135.0	0.00678	5.6
	x	0.950	2.676	3.582	159.7	0.00519	4.2
	y	0.980	2.507	3.175	125.3	0.00783	6.6

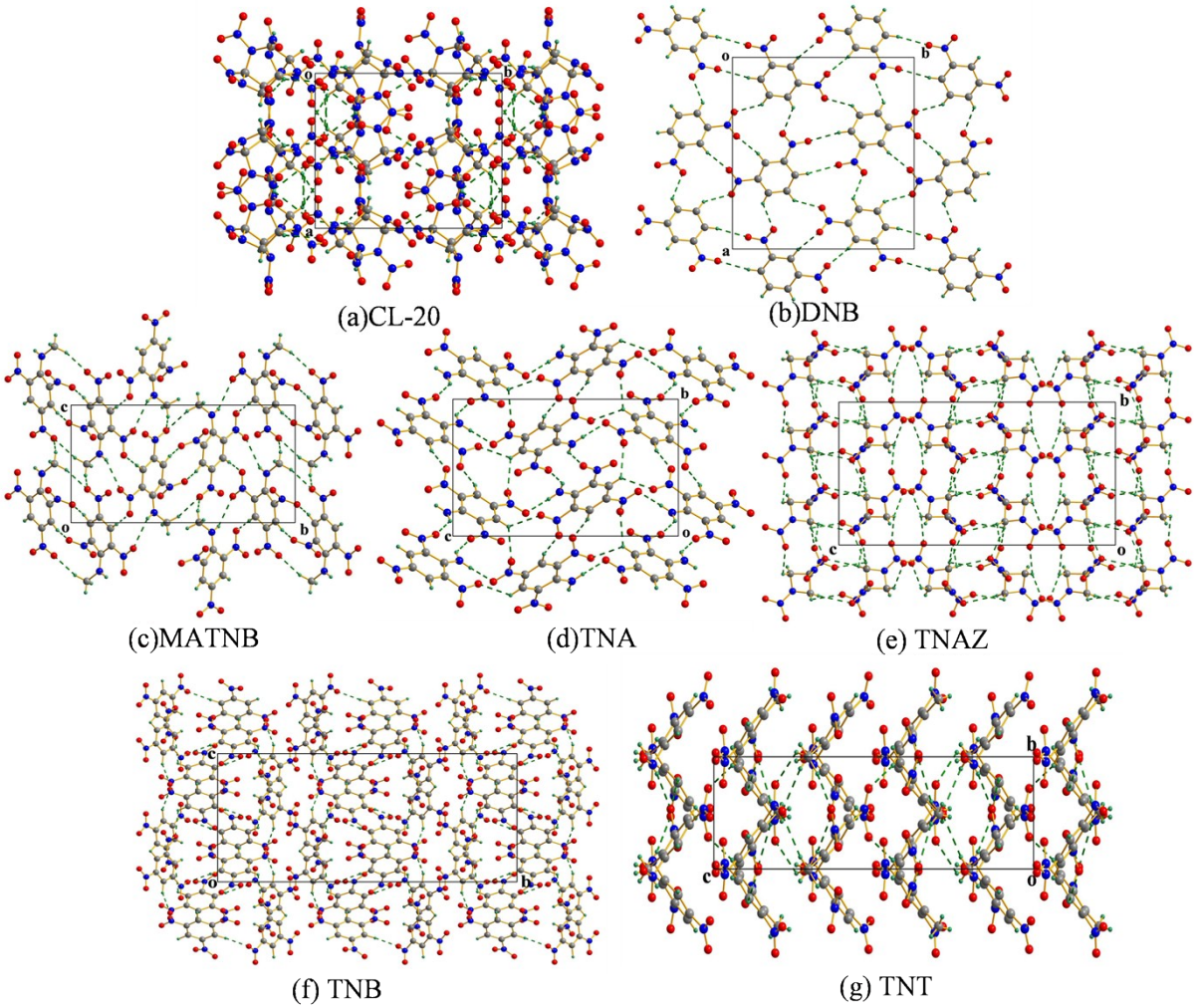

Fig. s2 HBs in the pure coformer crystals represented by green dash.

Table s3. Geometry and QTAIM analyses of the intermolecular HBs in pure coformer crystals.

Explosive	Number	D-H, Å	H···A, Å	A···D, Å	A-H···D,°	ρ, e/Å^3	E_{HB}, kJ/mol
CL-20	a1	0.896	2.621	3.177	121.0	0.00762	6.9
	a2	0.809	2.602	3.235	136.3	0.00723	6.0
	a3	0.961	2.660	3.306	124.9	0.00690	5.8
	a4	0.961	2.778	3.277	113.1	0.00591	5.3
	a5	0.961	2.503	3.275	137.3	0.00760	6.2
	a6	0.961	2.767	3.556	139.9	0.00348	2.9
DNB	b1	0.929	2.555	3.267	133.7	0.00722	5.9
	b2	0.930	2.635	3.497	154.3	0.00512	4.1
	b3	0.930	2.632	3.429	144.1	0.00640	5.1
	b4	0.930	2.689	3.573	158.8	0.00477	3.7
MATNB	c1	1.000	2.544	3.420	146.3	0.00755	6.0
	c2	0.942	2.674	3.507	147.7	0.00520	4.1
	c3	0.922	2.562	3.278	134.9	0.00726	6.0
	c4	0.925	2.565	3.136	120.4	0.00696	6.3
	c5	0.861	2.672	3.520	168.4	0.00531	4.0
TNA	d1	0.884	2.359	3.033	133.2	0.01068	9.3
	d2	0.984	2.546	3.245	127.9	0.00762	6.1
	d3	0.984	2.593	3.189	119.1	0.00670	5.6
	d4	0.924	2.379	3.153	135.8	0.00805	7.2
	d5	1.010	2.546	3.523	162.7	0.00589	4.6
TNAZ	e1	0.954	2.706	3.367	127.0	0.00510	4.2
	e2	0.940	2.792	3.731	177.0	0.00405	3.1
	e3	0.940	2.666	3.125	110.8	0.00705	5.9
	e4	1.058	2.676	3.286	116.3	0.00607	5.0
	e5	1.058	2.638	3.464	134.6	0.00668	5.3
	e6	0.940	2.762	3.239	112.4	0.00503	4.3
	e7	0.954	2.696	3.440	135.2	0.00503	4.1
TNB	f1	1.064	2.246	3.294	168.3	0.01169	9.4
	f2	1.165	2.281	3.369	154.3	0.0117	9.4
	f3	1.098	2.629	3.256	115.4	0.00765	6.1
TNT1	g1	1.079	2.540	3.516	150.0	0.00752	5.8
	g2	0.936	2.621	3.307	130.6	0.00614	5.0
	g3	1.083	2.382	3.429	162.2	0.00993	7.6
	g4	0.974	2.784	3.439	125.2	0.00516	4.3
	g5	1.033	2.631	3.347	126.3	0.00779	6.4
TNT2	h1	1.002	2.683	3.390	127.8	0.00557	4.5

	h2	1.083	2.382	3.429	162.2	0.00993	7.6
	h3	0.905	2.613	3.447	153.6	0.00603	4.8
	h4	0.983	2.701	3.490	137.5	0.00485	4.1
	h5	0.974	2.784	3.439	125.2	0.00516	4.3
	h6	1.033	2.631	3.347	126.3	0.00779	6.4

S3. Hirshfeld surface of BTF molecules involved in pure BTF crystal and the seven BTF-based EECCs.

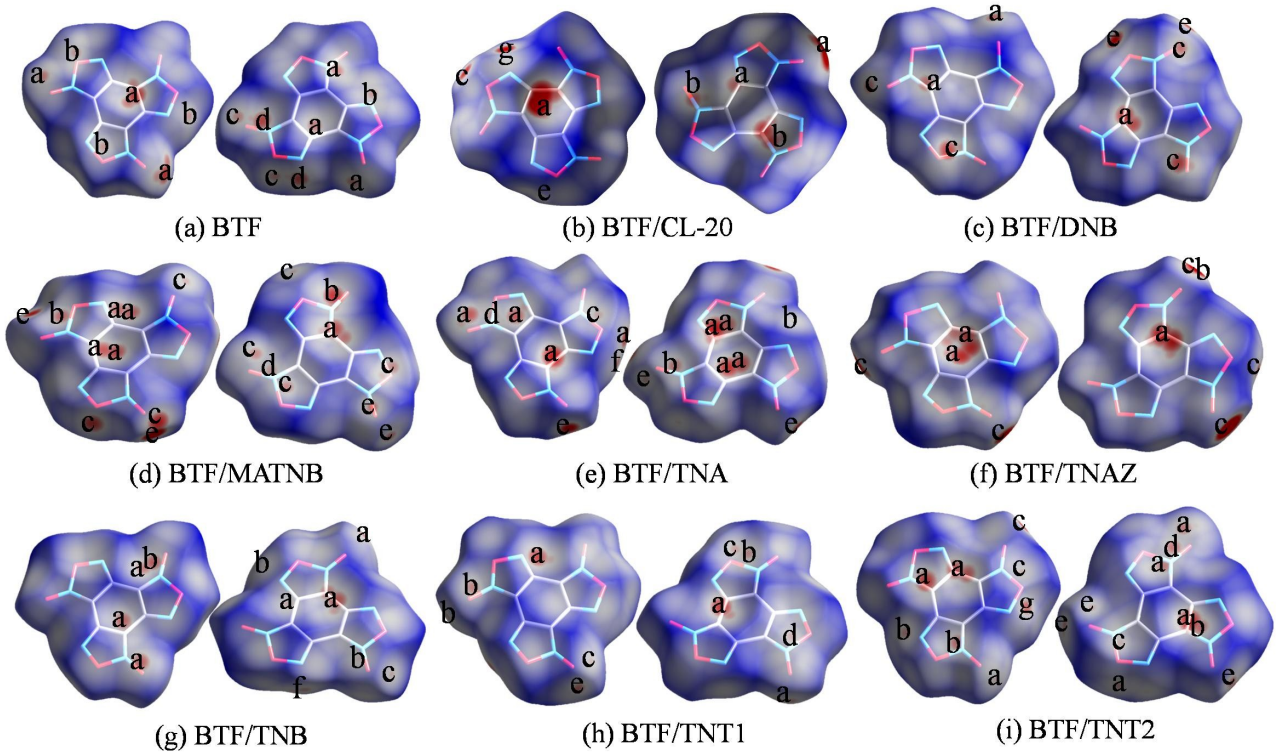

Fig. s3 Hirshfeld surfaces of BTF molecules in crystals, each shows by two plots with a torsion of 180°. Because BTF/TNT has Z′=2, the surfaces are illustrated by (h) and (i) separately. a-g denote the contacts of C···O, N···O, O···O, N···N, O···H, C···N, and N···H, respectively.

S4. References

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