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Supporting information for article:

Cocrystals assembled from iodoperfluorobenzene and flexible NTPO *via* halogen and π-hole bonds

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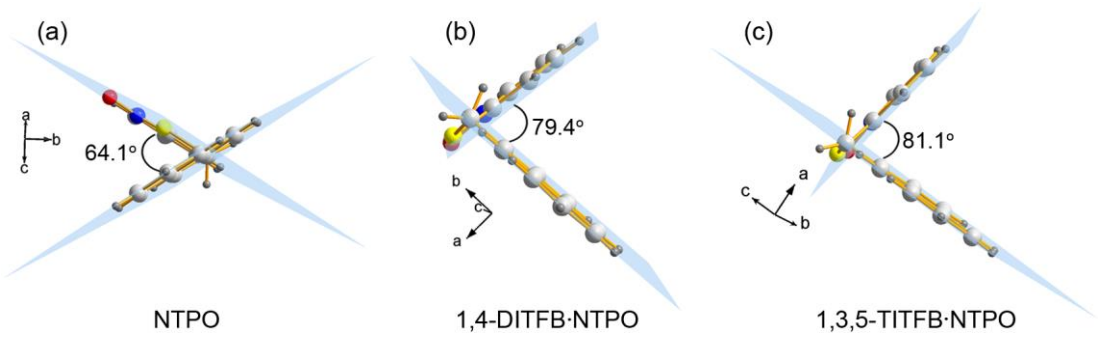

Figure S1 The torsion angle between pyridine ring and naphthalene ring of NTPO molecule in unary NTPO crystal, binary 1,4−DITFB·NTPO and 1,3,5−TITFB·NTPO cocrystals.

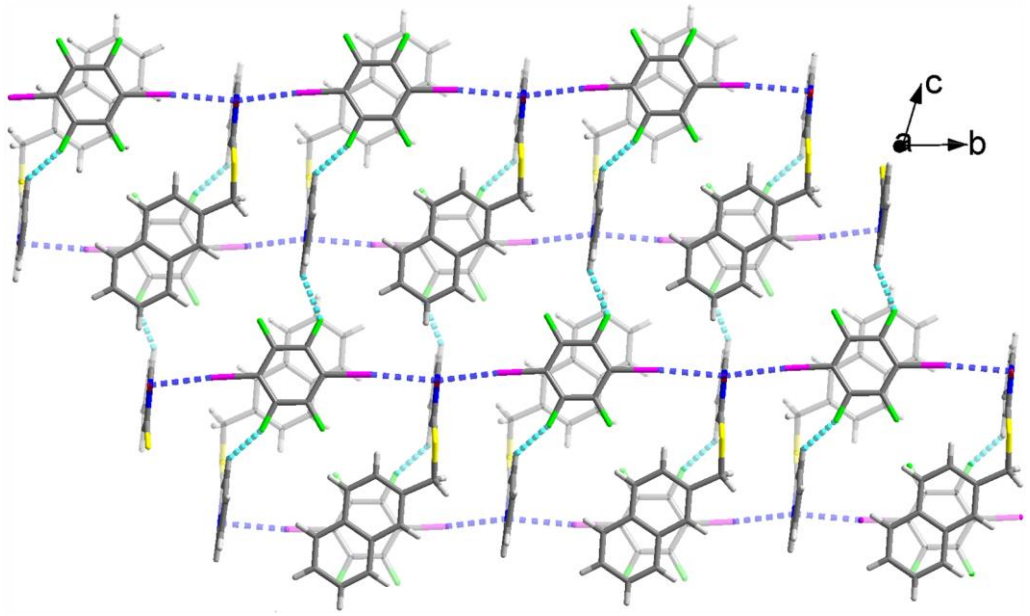

Figure S2 The 2D framework of 1,4−DITFB·NTPO cocrystal along the *bc* plane. For clarification, C, gray; H, white; O, red; N, blue; F, green; S, yellow; I, violet.

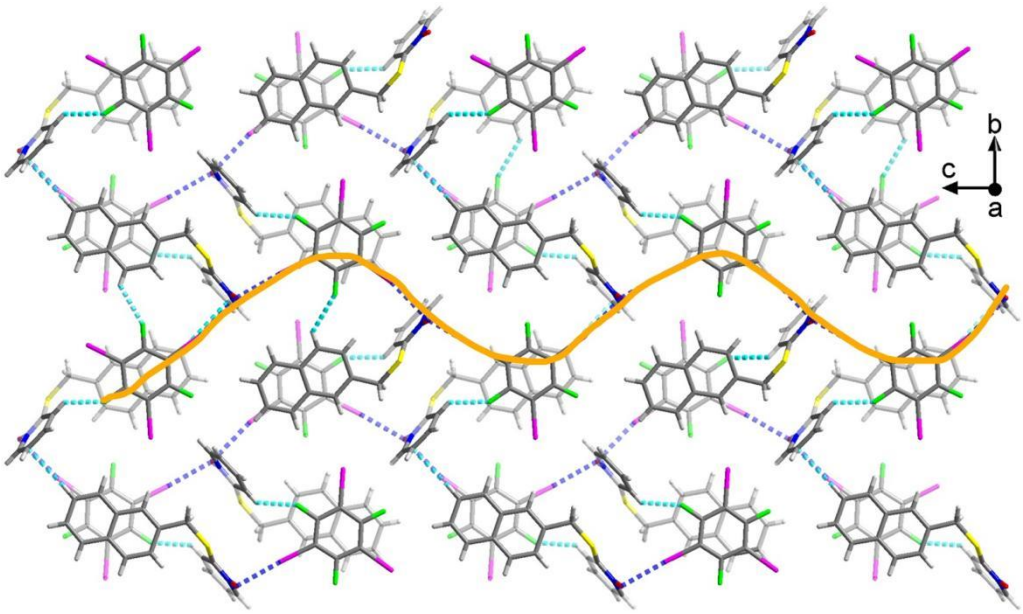

Figure S3 The 2D structure of 1,3,5−TITFB·NTPO cocrystal along the *bc* plane. For clarification, C, gray; H, white; O, red; N, blue; F, green; S, yellow; I, violet.

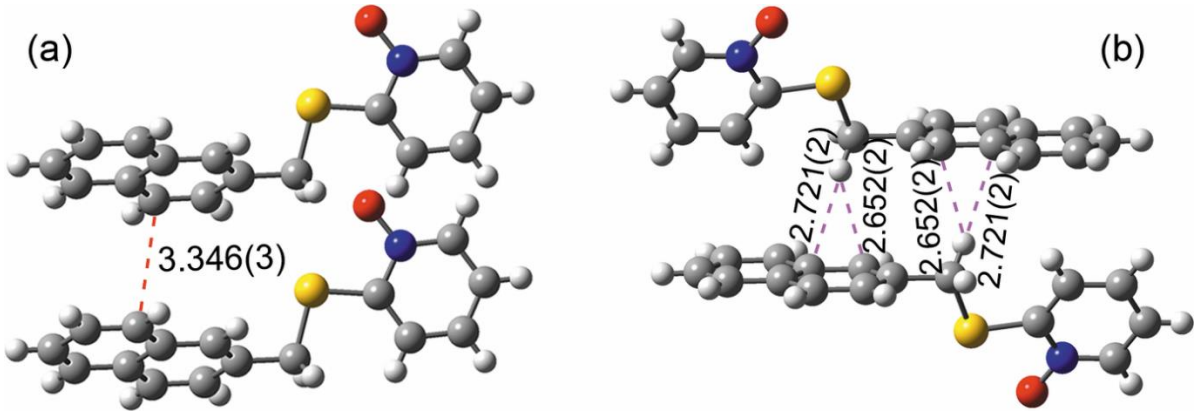

Figure S4 The details of π−π stacking (a) and C−H···π hydrogen bonds (b) interaction models in unary NTPO crystal for calculation. For clarification, C, gray; H, white; O, red; N, blue; S, yellow.

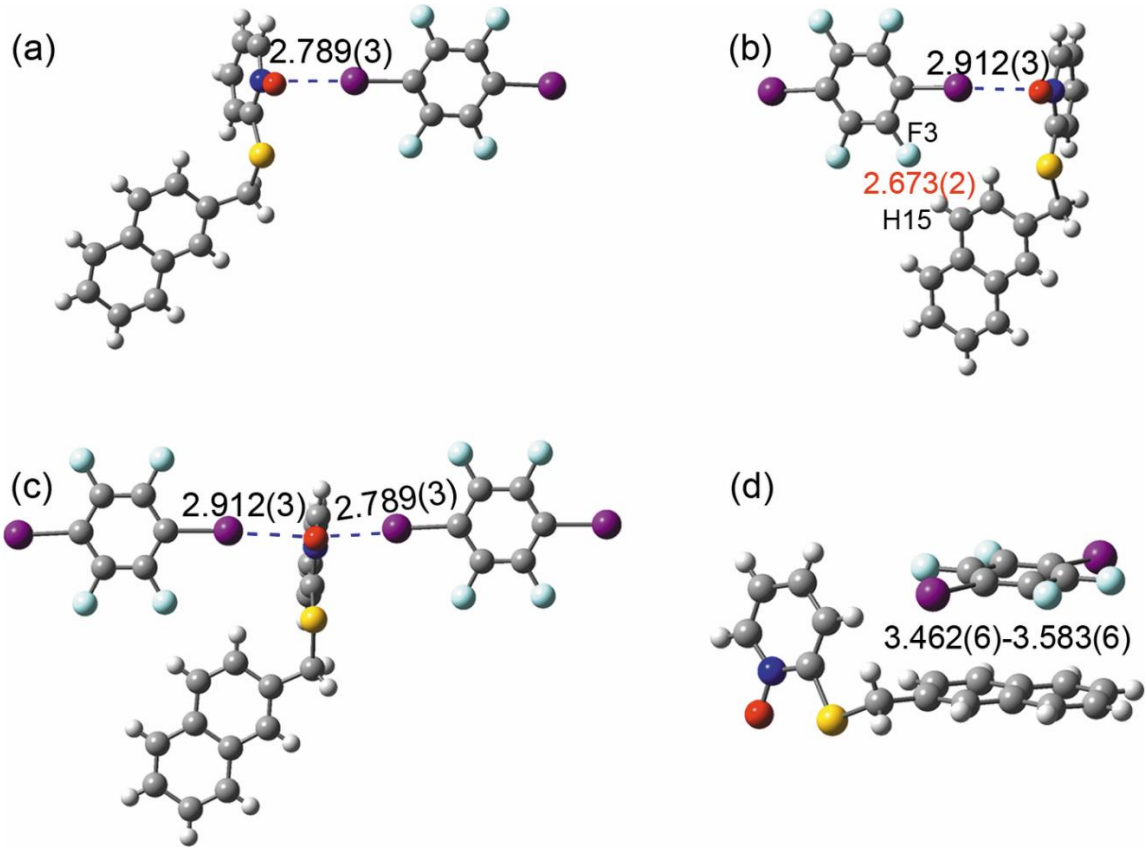

Figure S5 The details of monodentate C–I···$^{-}$O–N^{+} halogen bond (a) and (b), bidentate C–I···$^{-}$O–N^{+} halogen bonds (c), as well as π–hole···π bond interactions interaction models in binary 1,4–DITFB·NTPO cocrystal for calculation. For clarification, C, gray; H, white; O, red; N, blue; F, cyan; S, yellow; I, violet.

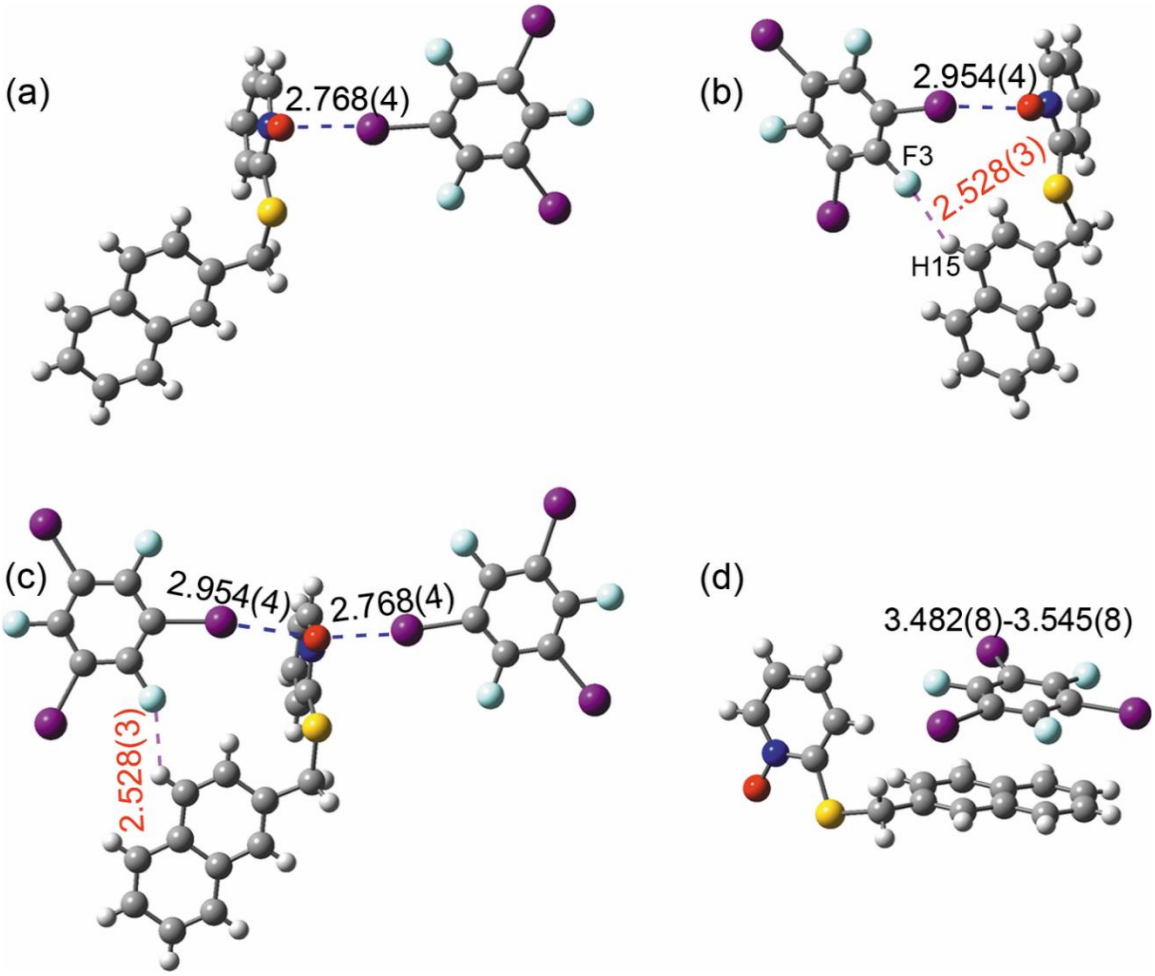

Figure S6 The details of monodentate C–I···$^{-}$O–N^{+} halogen bond (a) and (b), bidentate C–I···$^{-}$O–N^{+} halogen bonds (c), as well as π–hole···π bond interactions interaction models in binary 1,3,5−TITFB·NTPO cocrystal for calculation. For clarification, C, gray; H, white; O, red; N, blue; F, cyan; S, yellow; I, violet.

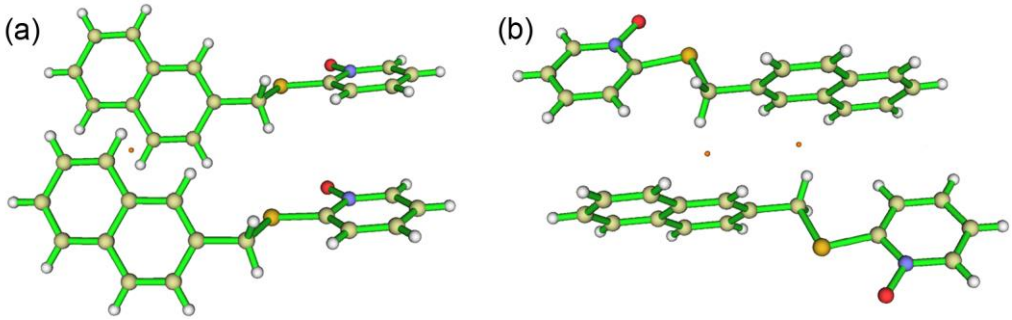

Figure S7 The intermolecular BCPs for the π−π stacking interaction (a) and C−H···π hydrogen bond (b) involved in unary NTPO crystal.

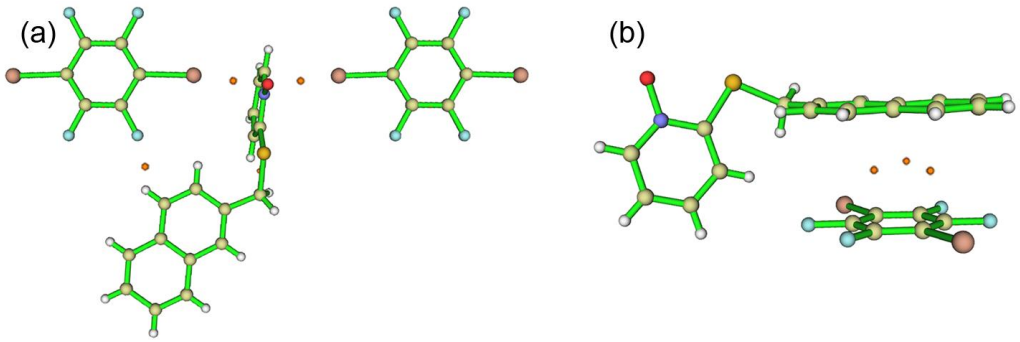

Figure S8 The intermolecular BCPs for C−I···$^{-}$O−N^{+} halogen bond, C−H···F hydrogen bond (a) and π−hole···π bond interactions (b) involved in binary 1,4−DITFB·NTPO cocrystal.

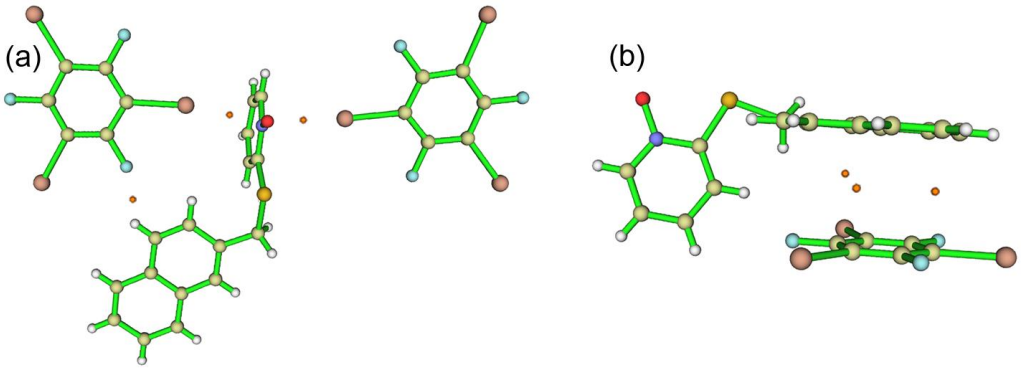

Figure S9 The intermolecular BCPs for C−I···$^{-}$O−N^{+} halogen bond, C−H···F hydrogen bond (a) and π−hole···π bond interactions (b) involved in binary 1,3,5−TITFB·NTPO cocrystal.

Table S1 The main bonding properties, geometrical parameters, interaction energies (ΔE, in kJ·mol^{-1}) obtained with the CP methods of unary and binary crystals.

Crystals	Interactions	*d*/Å	θ/°	ΔE/kJ·mol^{-1}
NTPO	π−π (C3···C8)	3.346 (3) −9.6%		−39.4
	C11−H11B···π(C1)	2.652 (2) −13.0%	133.25 (12)	−54.3
	C11−H11B···π(C2)	2.721 (2) −10.8%	147.73 (13)	
	C16−H16···O1	2.2395 (15) −17.7%	166.22 (15)	
	C6−H6···S1	2.8183 (6) −6.1%	144.28 (13)	
1,4−DITFB·NTPO	C17−I1···$^{-}$O1−N1^{+}	2.789 (3) −20.3%	172.53 (12)	−44.0
	C20−I2···$^{-}$O1−N1^{+}	2.912 (3) −16.8%	170.17 (13)	−40.5
	π−hole···π (C17···C8)	3.549 (6) −4.1%		−57.0
	π−hole···π (C17···C9)	3.583 (6) −3.2%		
	π−hole···π (C18···C9)	3.548 (6) −4.1%		
	π−hole···π (C18···C10)	3.552 (6) −4.0%		
	π−hole···π (C20···C13)	3.462 (6) −6.4%		
	π−hole···π (C20···C14)	3.582 (6) −3.2%		
	π−hole···π (C21···C14)	3.566 (6) −3.6%		
	π−hole···π (C21···C15)	3.526 (6) −4.7%		
	C3−H3···O1	2.511 (3) −7.7%	130.6 (3)	
	C11−H11···O1	2.600 (3) −4.4%	160.8 (3)	
	C3−H3···S1	2.8241 (9) −5.9%	153.1 (3)	
	C1−H1···F2	2.423 (2) −9.3%	125.5 (3)	
	C4−H4···F4	2.475 (2) −7.3%	137.4 (3)	
	C21−F3···F3−C21	2.848 (5) −3.1%	133.8 (3)	
1,3,5−TITFB·NTPO	C17−I1···$^{-}$O1−N1^{+}	2.768 (4) −20.9%	174.39 (16)	−38.7
	C21−I3···$^{-}$O1−N1^{+}	2.954 (4) −15.6%	166.77 (16)	−43.6
	π−hole···π (C17···C8)	3.523 (7) −4.8%		−60.0
	π−hole···π (C19···C14)	3.538 (8) −4.4%		
	π−hole···π (C21···C10)	3.536 (8) −4.4%		
	π−hole···π (C21···C11)	3.545 (8) −4.2%		
	π−hole···π (C22···C10)	3.482 (8) −5.9%		
	C4−H4···F1	2.524 (3) −5.5%	133.2 (3)	
	C15−H15···F3	2.528 (3) −5.3%	128.9 (4)	
	C3−H3···S1	2.7927 (12) −6.9%	145.8 (3)	
	C11−H11···π (C2)	2.834 (5) −7.1%	167.3 (4)	

The negative percentage is defined as the percentage reduction in interaction length relative to the sum of vdW radii of the two interacting atoms.

Table S2 The topological parameters at the intermolecular BCP for the unary and binary crystals. Computational levels: M06−2X/aug−cc−pVDZ; the topological parameters: ρ_b in e·Å^{-3}; $\nabla^2\rho_b$ in e·Å^{-5}; G_{BCP} and V_{BCP} in kJ·mol^{-1}·bohr^{-3}.

Crystals	BCP	ρ_b	$\nabla^2\rho_b$	G_{BCP}	V_{BCP}	H_{BCP}
NTPO	π−π (3.346 (3) Å)	0.038	0.369	7.892	−5.722	2.170
	C−H···π (2.652 (2) Å)	0.059	0.647	15.001	−12.369	2.633
1,4−DITFB·NTPO	C−I···$^{-}$O−N^{+} (2.789 (3) Å)	0.159	1.793	46.813	−46.899	−0.085
	C−I···$^{-}$O−N^{+} (2.912 (3) Å)	0.129	1.442	37.436	−36.800	0.636
	C−H···F (2.673 (2) Å)	0.032	0.570	12.176	−8.820	3.353
	π−hole···π (3.462 (6) Å)	0.038	0.354	8.318	−6.999	1.319
	π−hole···π (3.548 (6) Å)	0.035	0.311	7.373	−6.282	1.090
	π−hole···π (3.566 (6) Å)	0.035	0.305	7.302	−6.283	1.018
1,3,5−TITFB·NTPO	C−I···$^{-}$O−N^{+} (2.768 (4) Å)	0.165	1.861	48.709	−49.085	−0.376
	C−I···$^{-}$O−N^{+} (2.954 (4) Å)	0.119	1.336	34.498	−33.562	0.935
	C−H···F (2.528 (3) Å)	0.041	0.694	15.718	−12.522	3.196
	π−hole···π (3.523 (7) Å)	0.036	0.324	7.708	−6.599	1.110
	π−hole···π (3.536 (8) Å)	0.038	0.338	8.002	−6.808	1.194
	π−hole···π (3.538 (8) Å)	0.033	0.310	7.253	−6.055	1.198