Supplementary Information

Methylxanthines for Halogen Bonded Cocrystals with 1,4-Diiodotetrafluorobenzene: Green Synthesis, Structure, Photophysics and DFT Studies

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Figure S1. Structural models used in the simulations: a) cocrystals and b) Free xanthines.

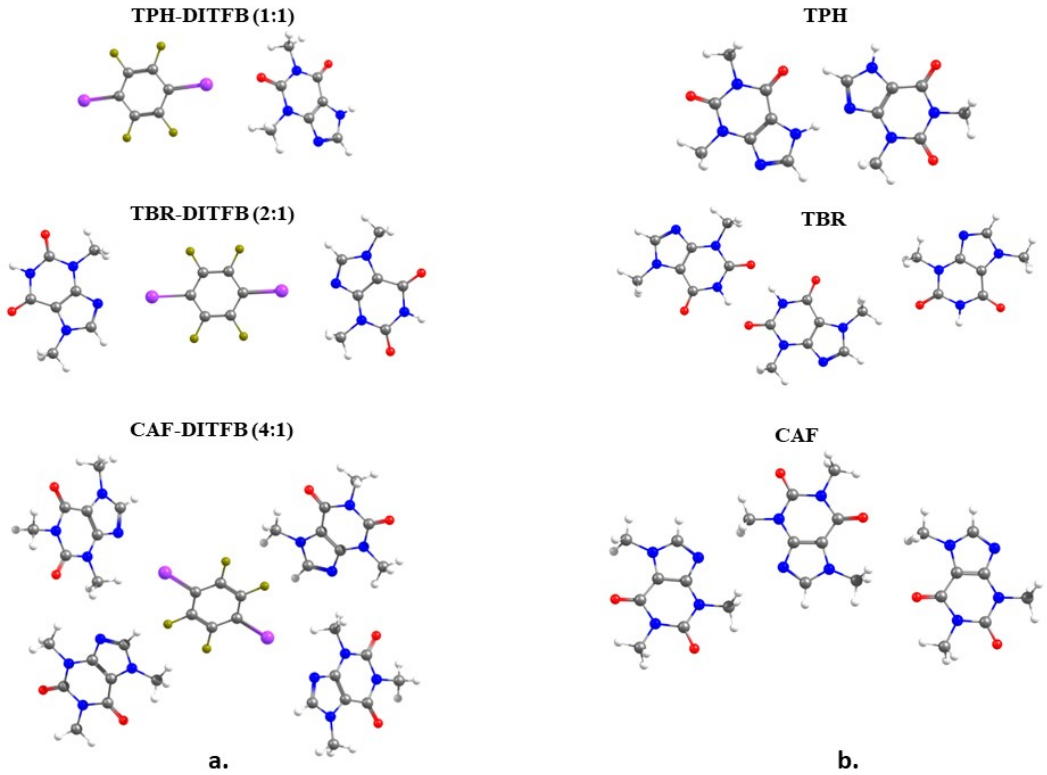


Table S1. Hydrogen-bond geometry (Å, º) for compounds **CAF-DITFB**, **TPH-DITFB** and **TBR-DITFB (2:1)**.

Compound	*D*—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
CAF-DITFB	C(14)-H(14C)···O(13)	0.96	2.48	3.097(13)	121.9
	C(28)-H(28)···O(11)#2	0.93	2.45	3.284(10)	149.6
	C(30)-H(30A)···O(31)#3	0.96	2.53	3.449(10)	161.4.0
	C(30)-H(30C)···O(31)#4	0.96	2.60	3.217(10)	122.2
	C(32)-H(32A)···I(1)	0.96	3.15	3.954(9)	141.9
	C(34)-H(34A)···O(11)#2	0.96	2.57	3.456(11)	153.1
TPH-DITFB	N(7)-H(7)···O(6)^{i}	0.86	1.93	2.778 (4)	167.3
	C(1)-H(1*A*)···O(2)^{ii}	0.96	2.53	3.425 (5)	155.9
	C(1)-H(1*B*)···O(2)^{iii}	0.96	2.63	3.227 (5)	120.4
	C(3)-H(3*A*)···I(1)^{iv}	0.96	3.35	4.067 (4)	132.8
	C(3)-H(3*B*)···I(2)^{v}	0.96	3.33	4.176 (4)	148.9
TBR-DITFB (2:1)	N(1)-H(1)...O(6)#1	0.86	2.03	2.887(6)	175.7
	C(7)-H(7A)...O(2)#2	0.96	2.31	3.245(8)	165.1
	C(7)-H(7C)...O(6)#3	0.96	2.63	3.544(8)	158.8

D-H: donor; A: acceptor
Symmetry codes for cocrystal **CAF-DITFB**: #1 -x+1,-y+2,-z+1 #2 -x+1,y+1/2,-z+3/2 #3 -x,y+1/2,-z+1/2 #4 -x,y-1/2,-z+1/2
cocrystal **TPH-DITFB**: (i) −*x*+1, −*y*+1, −*z*+2; (ii) −*x*+1/2, *y*−1/2, −*z*+3/2; (iii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iv) *x*, *y*+1, *z*; (v) −*x*+1, −*y*+1, −*z*+1.

cocrystal **TBR-DITFB (2:1)**: #1 -x+1,-y+1,-z+2 #2 x-1,y-1,z #3 -x+1,-y,-z+2

Figure S2. TGA-DSC of the cocrystal **CAF-DITFB**.

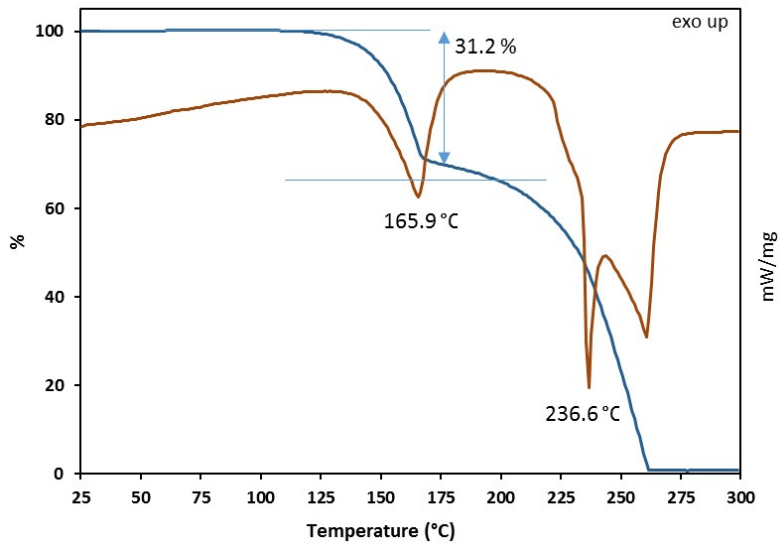


Figure S3. a) TGA-DSC trace of cocrystal **TPH-DITFB** and b) phase transformation between theophylline and its cocrystal.

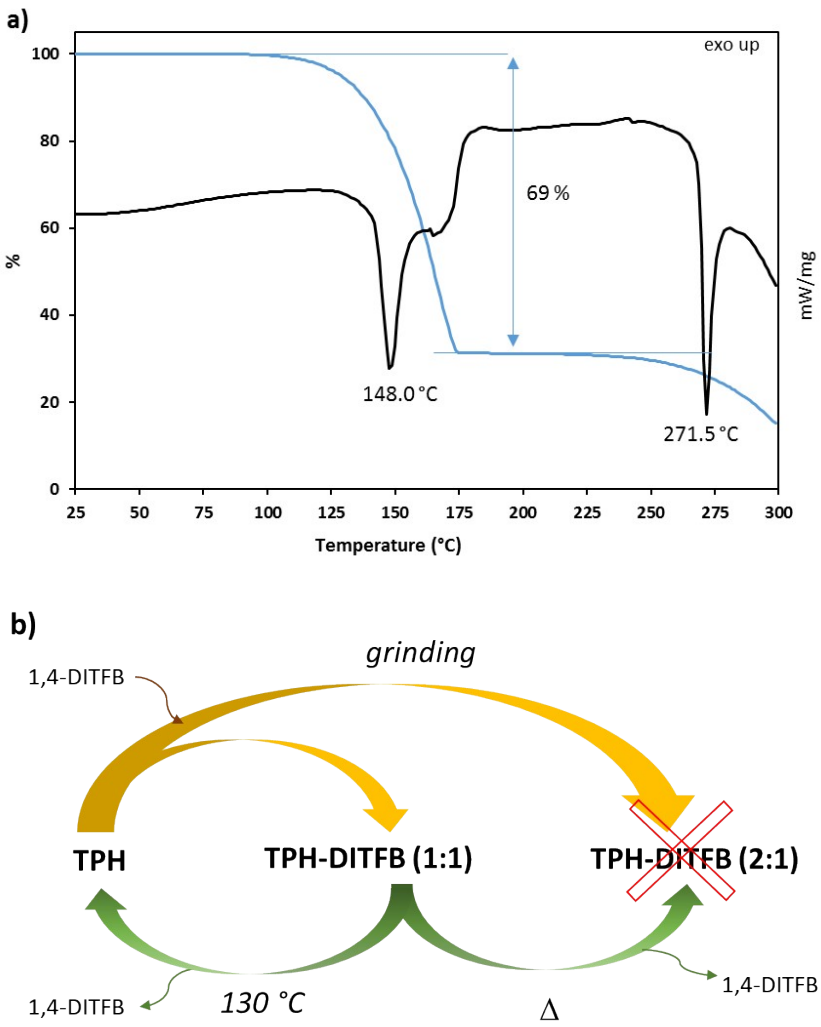
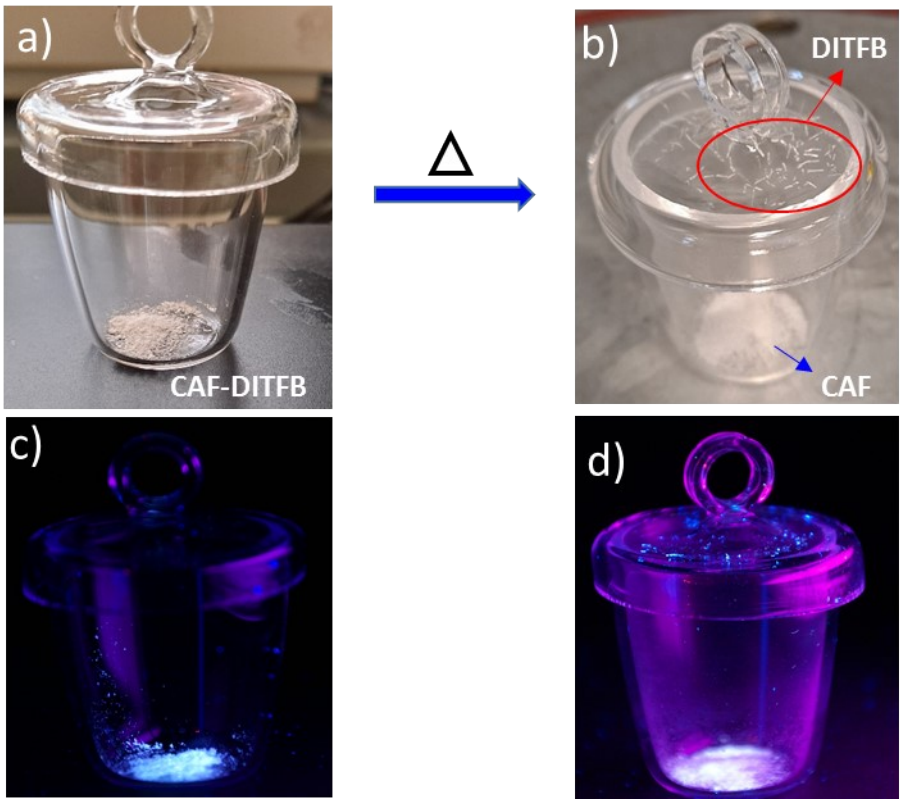
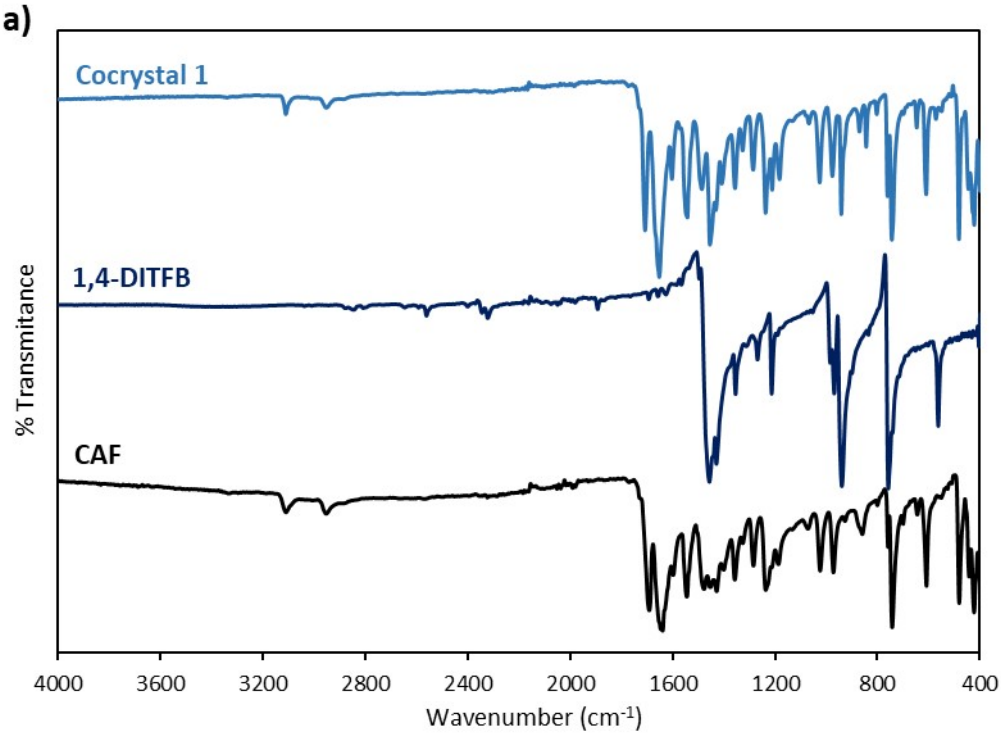


Figure S4. Transformation process by heating **CAF-DITFB** cocrystal (left) to **CAF** (right). Optical images under visible light (a and b) and under UV (365 nm) (c and d). Under UV the off-on transformation could be observed.



Figures S5. FTIR spectra of natural xanthines, coformer **DITFB** and their cocrystals.



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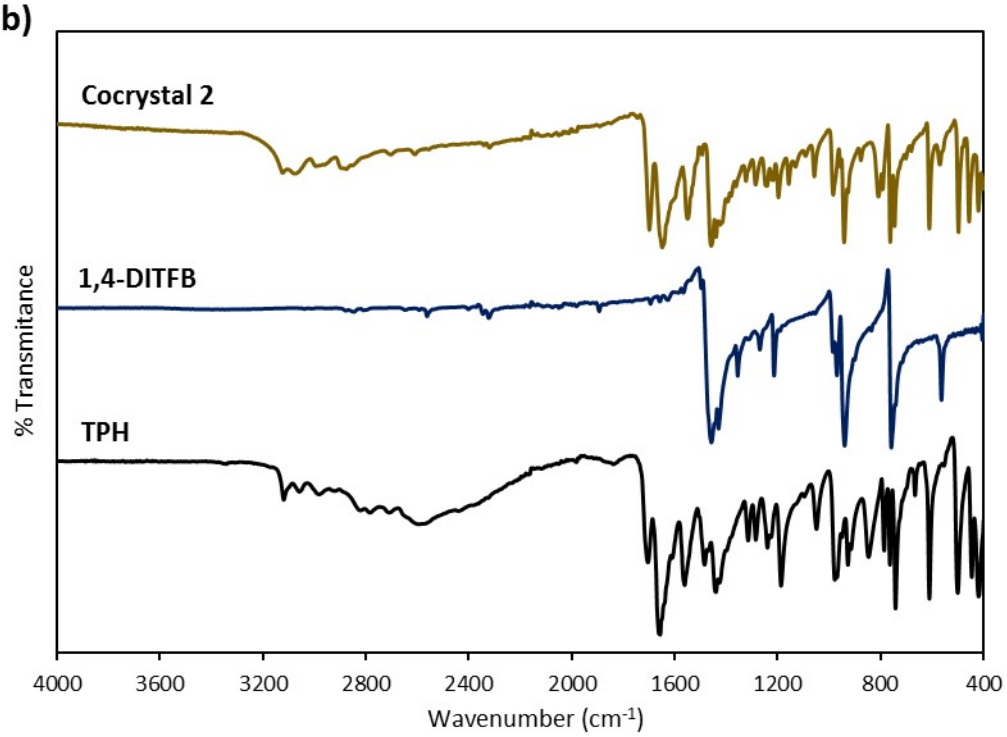

Cocrystal 2
1,4-DITFB
TPH
% Transmitance
4000
3600
3200
2800
2400
2000
1600
1200
800
400
Wavenumber (cm-1)

c)

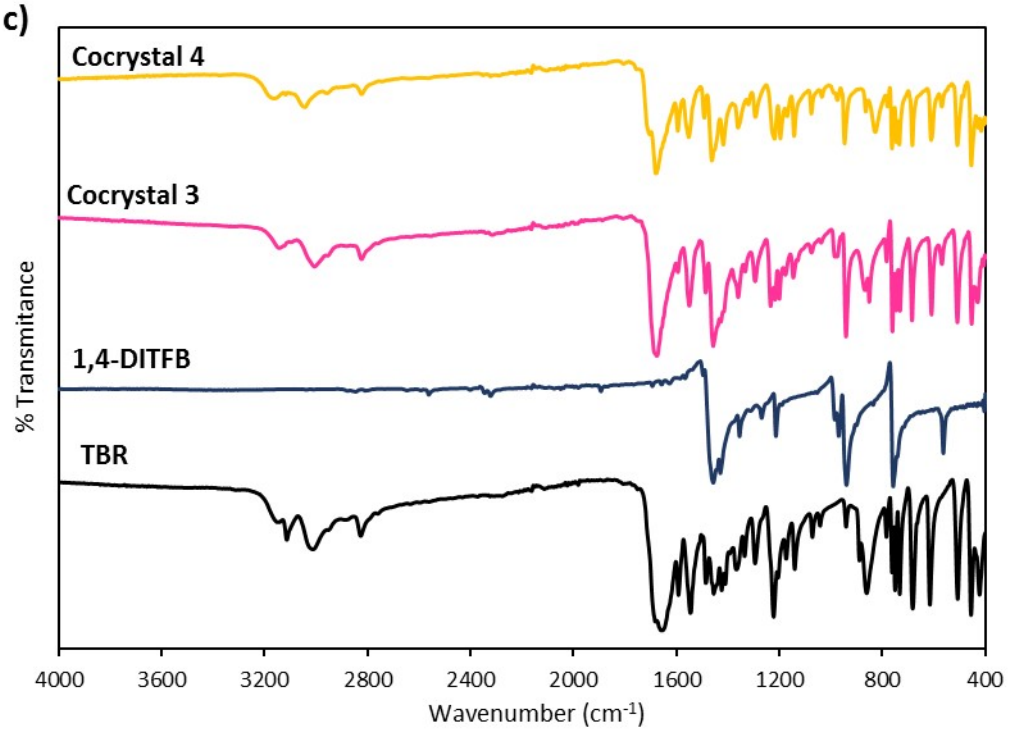

Cocrystal 4
Cocrystal 3
1,4-DITFB
TBR
% Transmitance
4000
3600
3200
2800
2400
2000
1600
1200
800
400
Wavenumber (cm-1)

Table S2. Summary of characteristic vibrational modes of the studied xanthines and coformer **DITFB**.

Vibrational mode	**DITFB**	**CAF**	**CAF-DITFB**	**TPH**	**TPH-DITFB**	**TBR**	**TBR-DITFB (1:1)**	**TBR-DITFB (2:1)**
ν_{C-C} stretch	1456	-	1453	-	1458	-	1456	1461
$\nu_{C—F}$ stretch.	937	-	940	-	943	-	940	943
$\nu_{C—I}$ asymm.	755	-	743	-	761	-	758	761
$\nu_{C=O}$; $\nu_{C=N}$	-	1691; 1640	1707; 1651	1704; 1657	1699; 1645	1657; 1592	1675	1704; 1678
$\nu_{N—H}$	-	3113; 2955	3113; 2950	3118;3057; 2984	3123; 3075; 2998	3150; 3115; 3016; 2827	3139; 3005; 2824	3164; 3043; 2955; 2824

Figure S6. Absorption and fluorescent emission spectra of **TPH** and **TPH-DITFB** cocrystal (a and b).

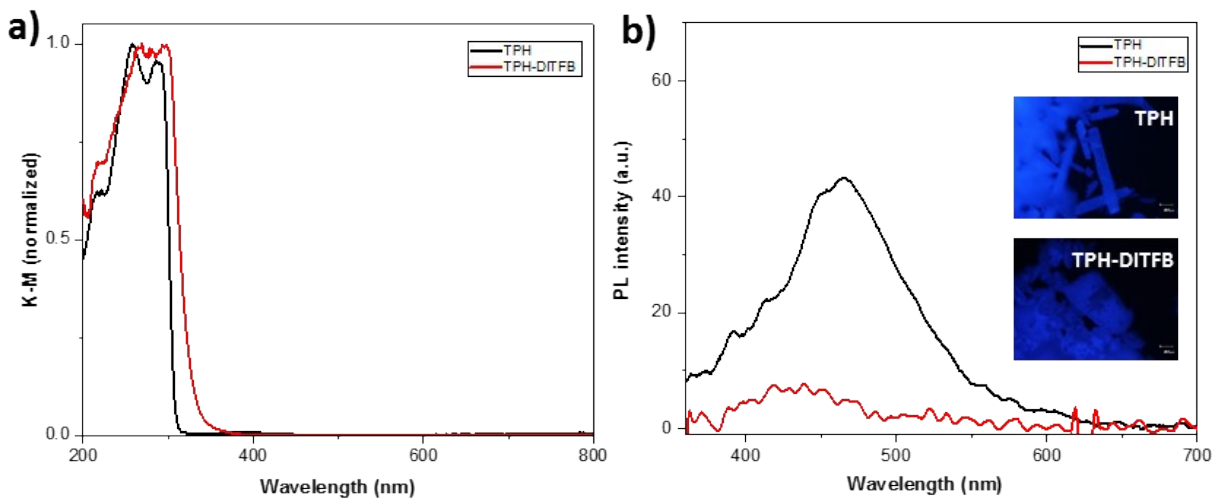


Table S3. Comparison of experimental and theoretical calculated cell parameters.

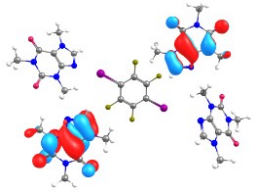
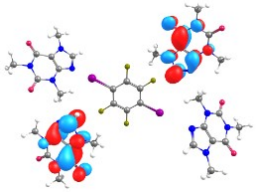
Parameters	CAF-DITFB		TPH-DITFB		TBR-DITFB (2:1)	
	Cryst data	Theo data	Cryst data	Theo data	Cryst data	Theo data
a (Å)	21.904(18)	21.924385	19.924(8)	19.821105	4.0269(18)	4.102633
b (Å)	4.044(4)	4.113429	4.4267(18)	4.451576	7.451(3)	7.422291
c (Å)	25.87(2)	25.756875	20.419(8)	20.357605	20.660(9)	20.589755
α (°)	90	90	90	90	82.022(8)	81.994578
β (°)	110.90(2)	110.996125	113.293(9)	113.367412	80.671(9)	80.634592
γ (°)	90	90	90	90	88.669(8)	88.664453

Table S4. X-bond interaction with distances and angles for the optimized cocrystals through periodic DFT calculations.

Cocrystal	I···N	d(I···N) (Å)	(C-I···N) (°)
CAF-DITFB *	I(1)···N(29)	2.859	175.41
CAF-DITFB (Periodic-DFT)	I···N	2.803	174.40
TPH-DITFB*	I(1)···N(9)	2.983	177.19
TPH-DITFB (Periodic-DFT)	I···N	2.90	176.73
TBR-DITFB (2:1) *	I(9)···N(9)	3.034	176.02
TBR-DITFB (Periodic-DFT)	I···N	2.957	175.094

*Labeling of N and I atoms refer to the labeling of these atoms in the main text.

Table S5. Surfaces of the molecular orbital (MOs) with their energies (eV), PBE0/ def2-TZPP theoretical level.

System	λ(nm)	*f*	Assignment	Active Molecular Orbital		
CAF-DITFB	257	0.32	$\pi^{(CAF)} \rightarrow \pi^{*\,(CAF)}$		→	
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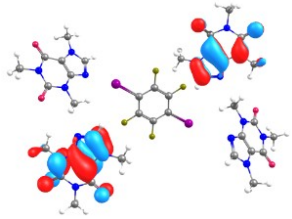
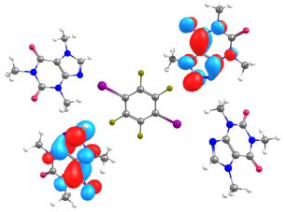
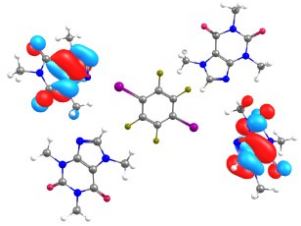
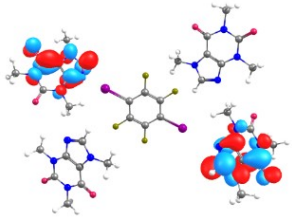
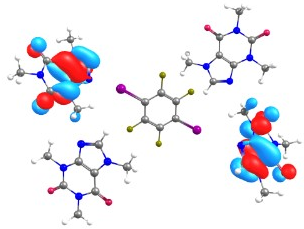
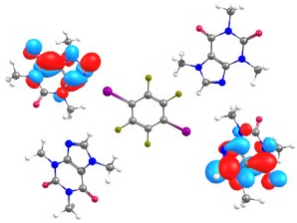
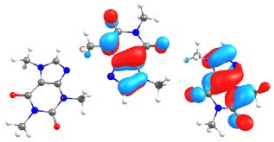
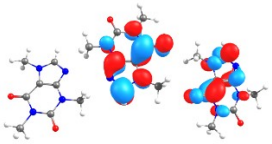
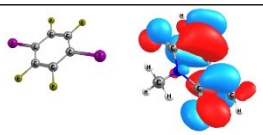
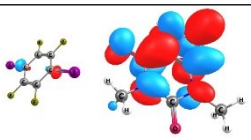
					→	
				H		L+7
	256	0.43	$\pi^{(CAF)} \rightarrow \pi^{*\,(CAF)}$		→	
				H-3		L+4
					→	
				H-2		L+5
CAF	259	0.52	$\pi^{(CAF)} \rightarrow \pi^{*\,(CAF)}$		→	
				H-1		L
TPH-DIFTB	249	0.29	$\pi^{(TPH)} \rightarrow \pi^{*\,(TPH)}$		→	
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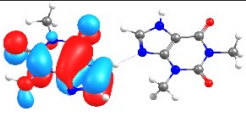
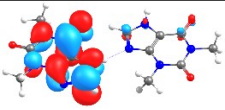
TPH	255	0.23	$\pi^{(TPH)} \rightarrow \pi^{*\,(TPH)}$		→	
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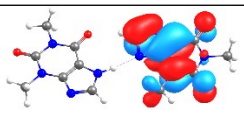
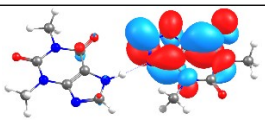
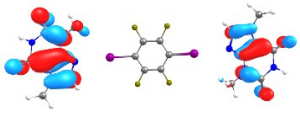
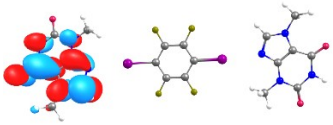
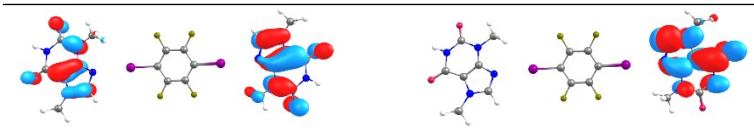
	251	0.18	$\pi^{(TPH)} \rightarrow \pi^{*\,(TPH)}$			
				H-1		L
TBR-DIFTB	255	0.67	$\pi^{(TBR)} \rightarrow \pi^{*\,(TBR)}$			

			$\pi^{(TBR)} \rightarrow \pi^{*\,(TBR)}$	H-1	L
					
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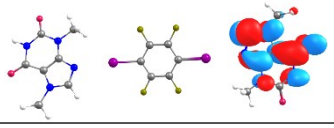
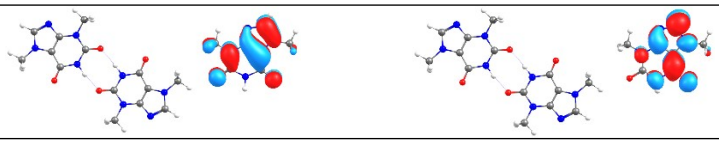
	239	0.23	$\pi^{(TBR)} \rightarrow \pi^{*\,(TBR)}$		
				H-1	L+1
TBR	251	0.14	$\pi^{(TBR)} \rightarrow \pi^{*\,(TBR)}$		
				H-2	L
	247	0.28	$\pi^{(TBR)} \rightarrow \pi^{*\,(TBR)}$		
				H	L+2

Figure S7. Energy diagrams for the most probable emission pathways in free xanthines. ISC, intersystem crossing.

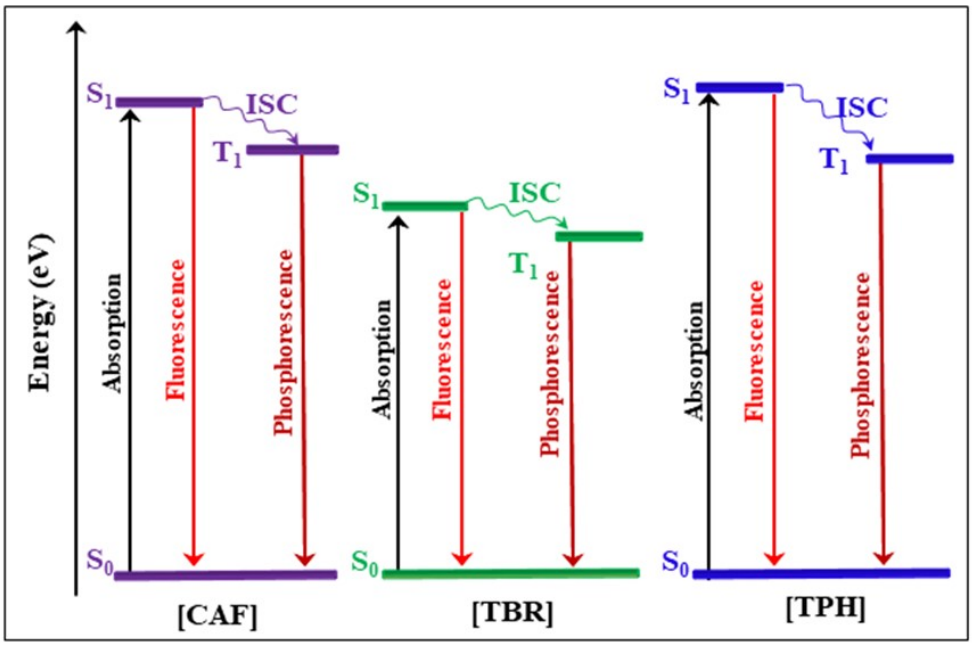
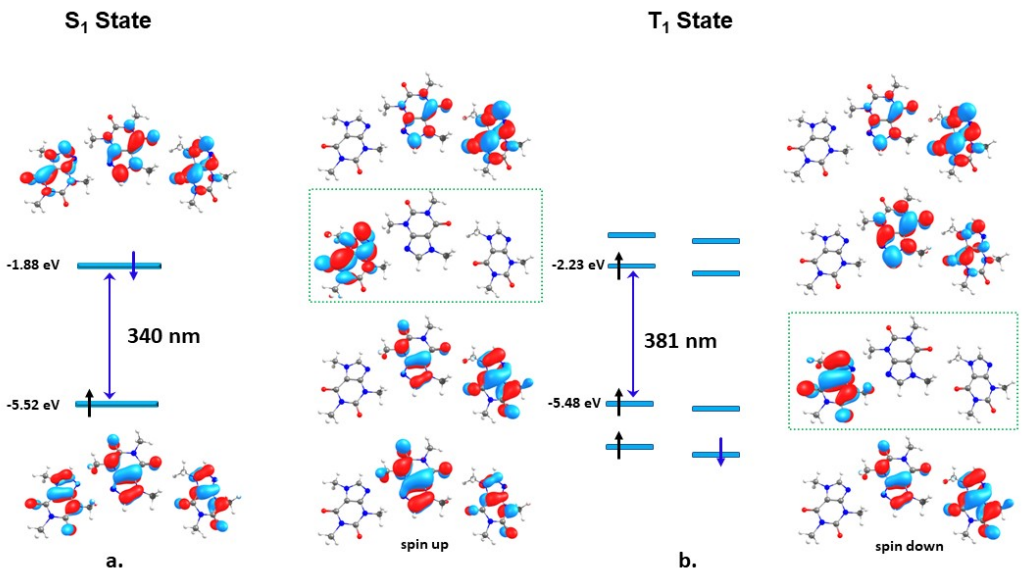


Figure S8. Frontier molecular orbitals of **CAF** based on the configurations of first electronic excited state. a. FMO of **CAF** in the S_1 electronic state. b. FMO of **CAF** in the T_1 electronic state. MO involved in these emissive states of the T_1 electronic state are dotted by green lines.



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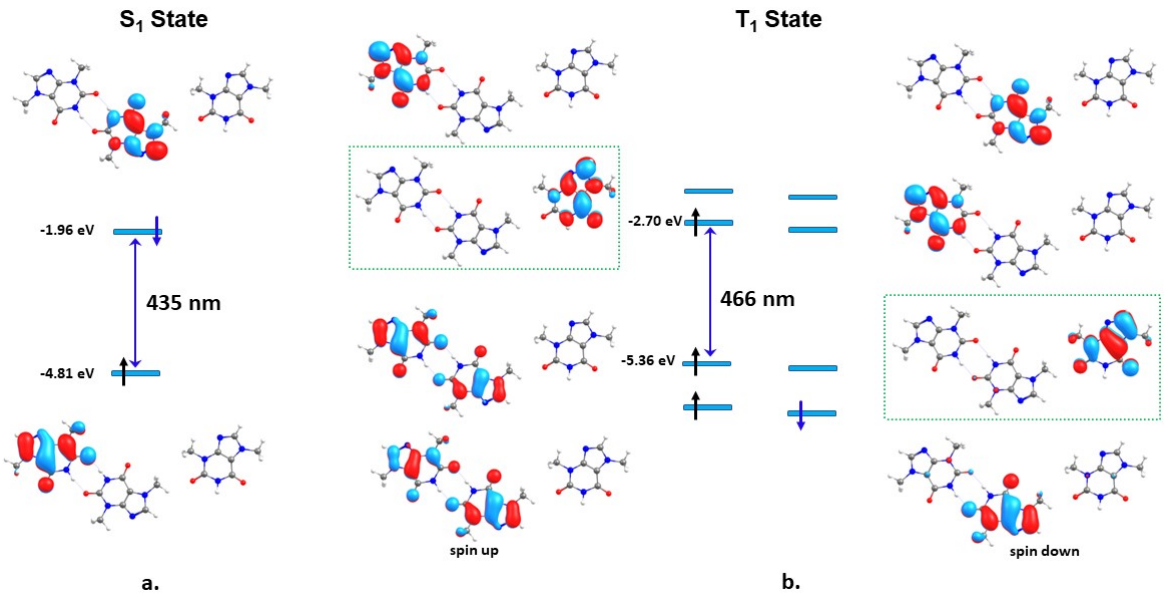

Figure S10. Frontier molecular orbitals of theophylline (**TPH**) based on the configurations of first electronic excited state. a. FMO of **TPH** in the S_1 electronic state. b. FMO of **TPH** in the T_1 electronic state. MO involved in these emissive states of the T_1 electronic state are dotted by green lines.

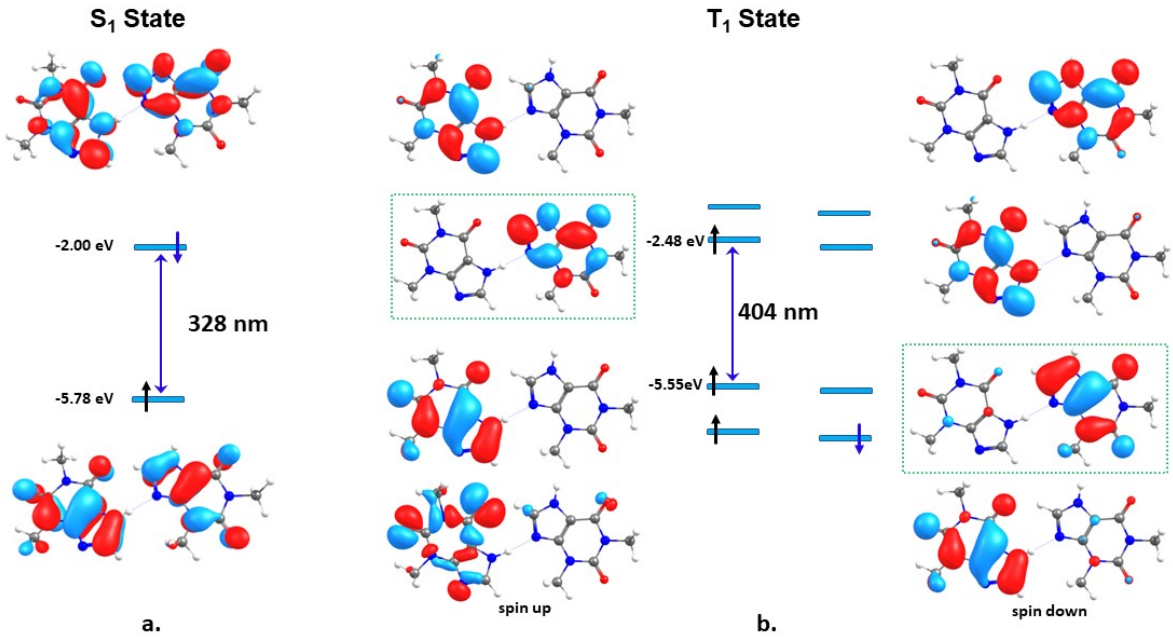

Figure S11. Frontier molecular orbitals of cocrystals based on the configurations of ground electronic excited state. a. FMO of **CAF-DITFB** in the S_0 electronic state. b. FMO of **TPH-DITFB** in the S_0 electronic state. c. FMO of **TBR-DITFB** in the S_0 electronic state.

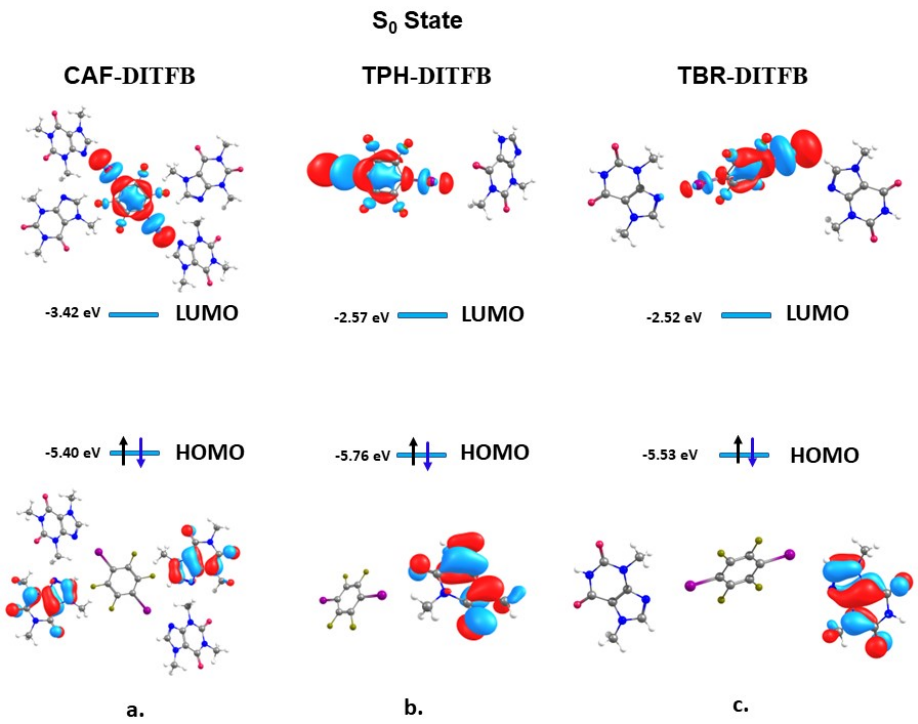

Figure S12. Energy diagrams for the most probable emission pathways in cocrystals. ISC, intersystem crossing.

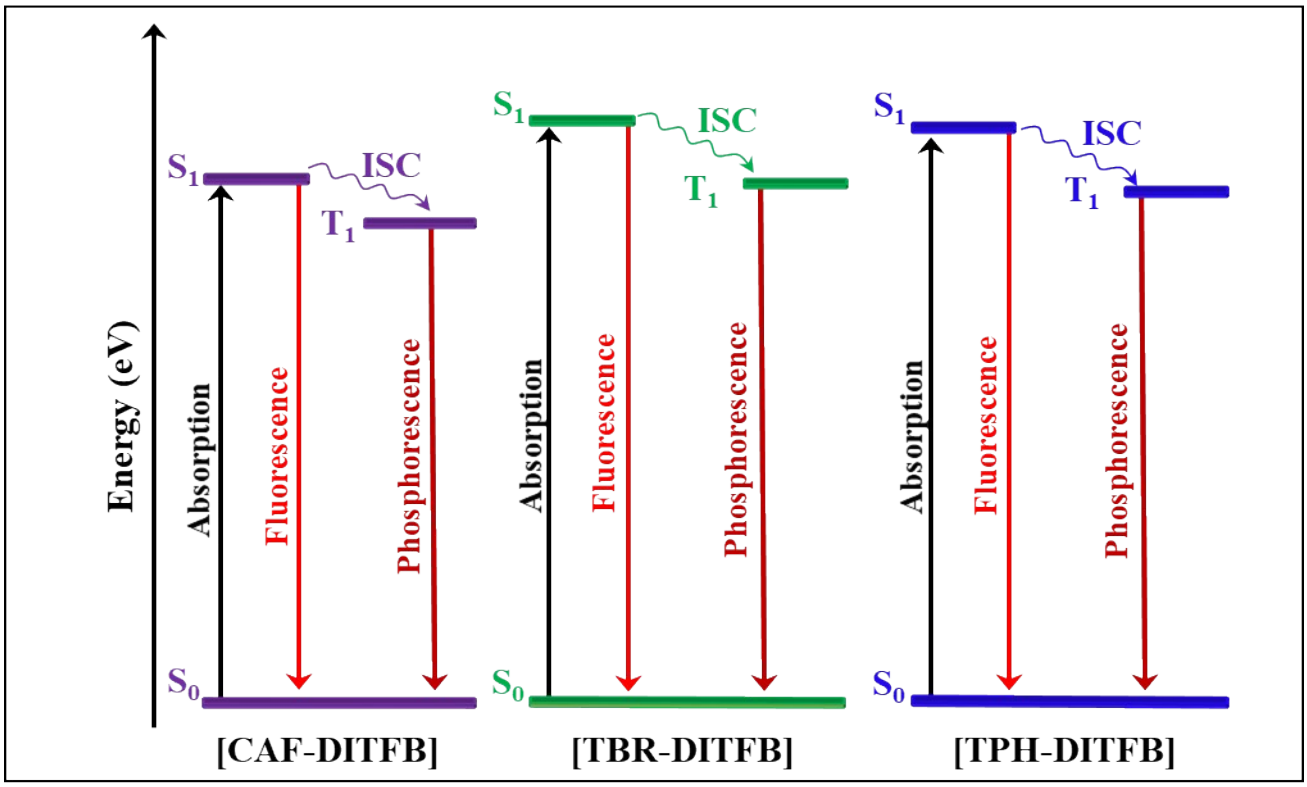

Figure S13. Frontier molecular orbitals of cocrystals **CAF-DITFB** based on the configurations of first electronic excited state. a. FMO of **CAF-DITFB** in the S_1 electronic state. b. FMO of **CAF-DITFB** in the T_1 electronic state. MO involved in these emissive states of the T_1 electronic state are dotted by green lines.

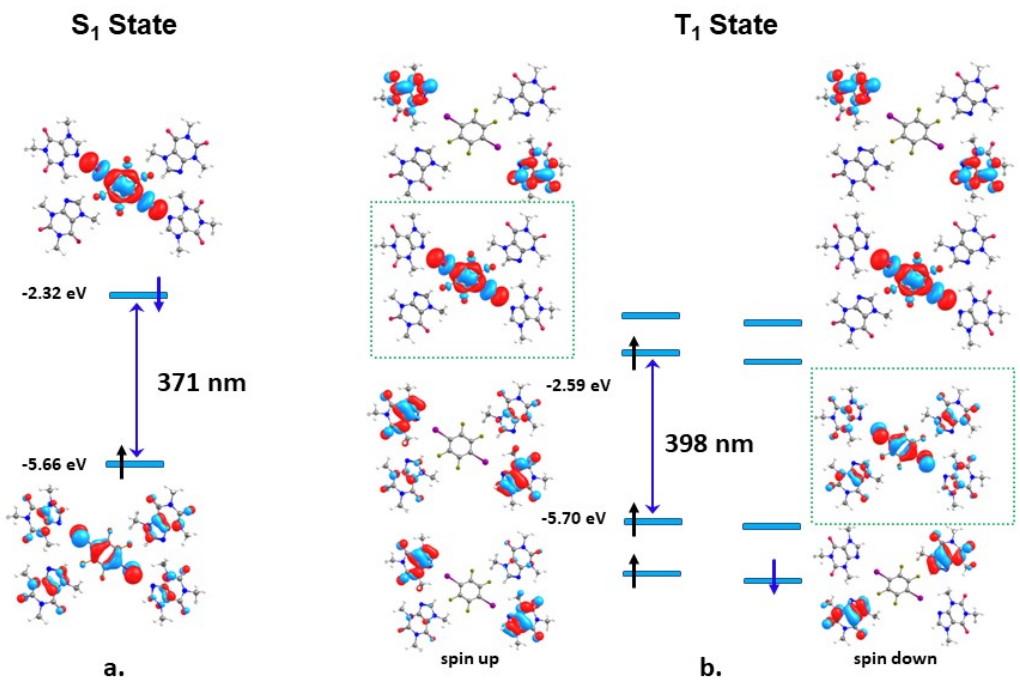

Figure S14. Frontier molecular orbitals of cocrystals **TPH-DITFB** based on the configurations of first electronic excited state. a. FMO of **TPH-DITFB** in the S_1 electronic state. b. FMO of **TPH-DITFB** in the T_1 electronic state. MO involved in these emissive states of the T_1 electronic state are dotted by green lines.

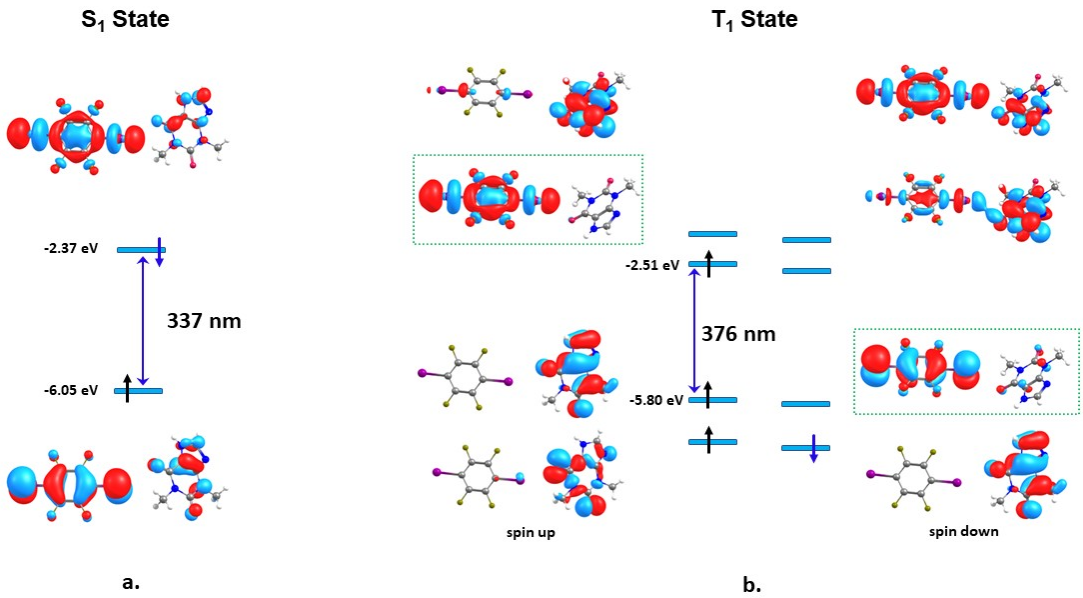

Figure S15. Frontier molecular orbitals of cocrystals **TBR-DITFB** based on the configurations of first electronic excited state. a. FMO of **TBR-DITFB** in the S_1 electronic state. b. FMO of **TBR-DITFB** in the T_1 electronic state. MO involved in these emissive states of the T_1 electronic state are dotted by green lines.