crystals

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Article

Tautomeric Equilibrium of an Asymmetric β-Diketone in Halogen-Bonded Cocrystals with Perfluorinated Iodobenzenes

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1. Figure S1–S29

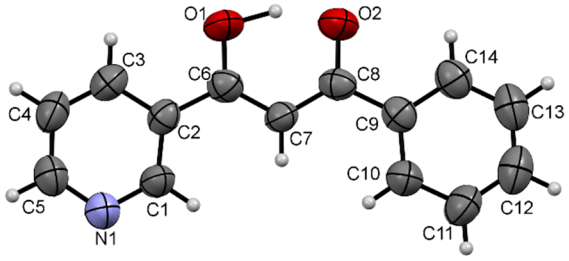

Figure S1. Molecular structure of **b3pm** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

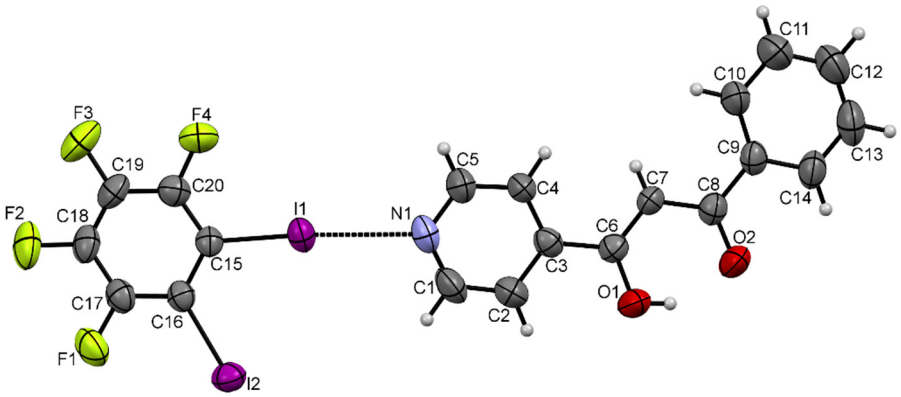

Figure S2. Molecular structure of (**b4pm**)(**13tfib**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

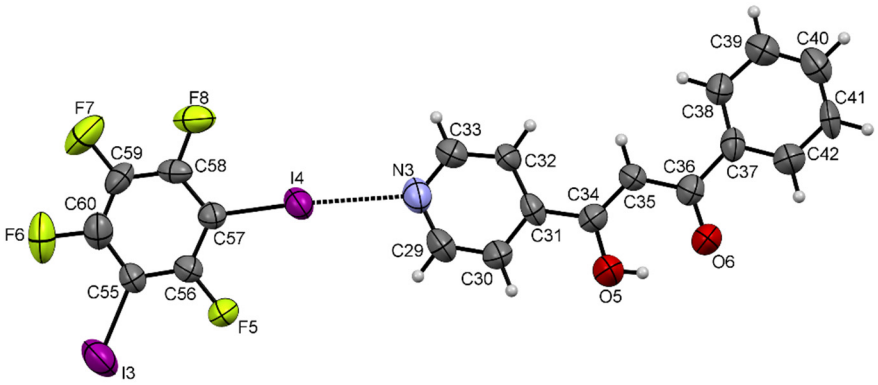

Figure S3. Molecular structure of **(b4pm)(13tfib)** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

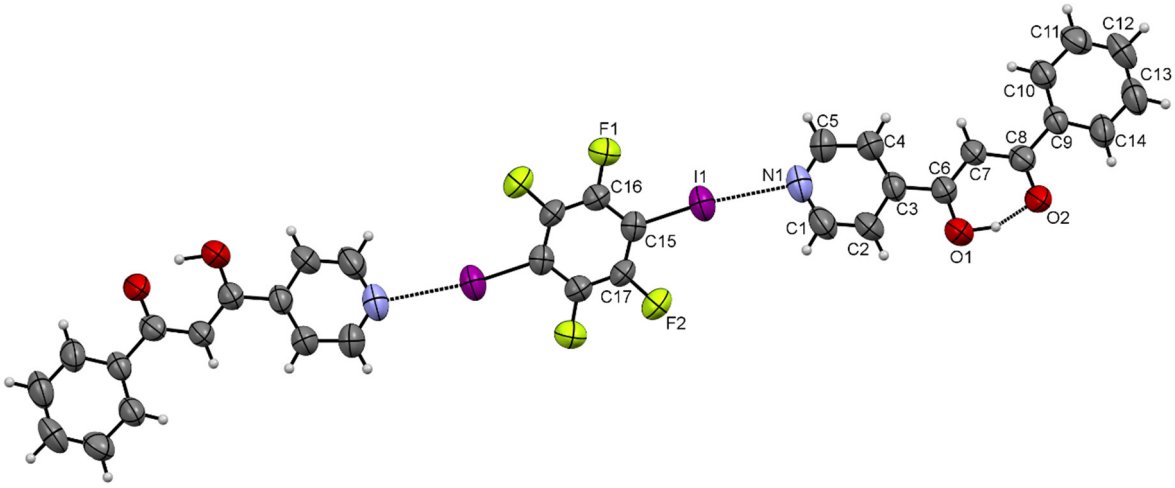

Figure S4. Molecular structure of **(b4pm)$_2$(14tfib)** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

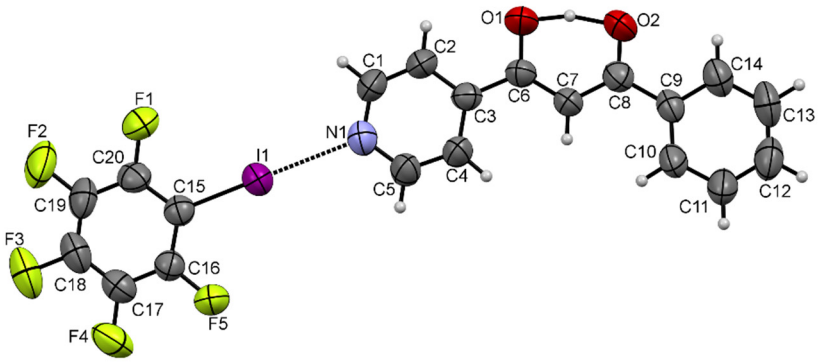

Figure S5. Molecular structure of (**b4pm**)(**ipfb**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

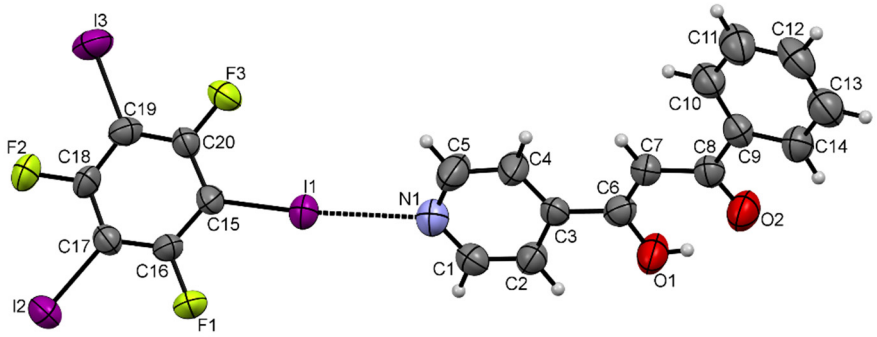

Figure S6. Molecular structure of (**b4pm**)(**135tfib**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

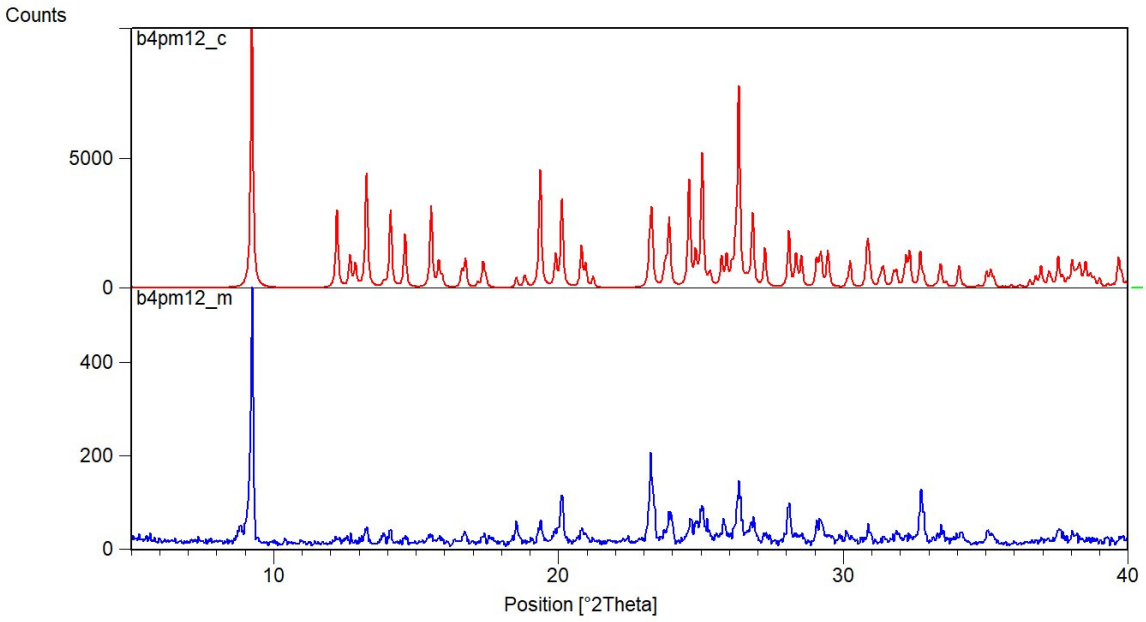

Figure S7. Measured (blue) and calculated (red) PXRD patterns of (**b4pm**)(**12tfib**).

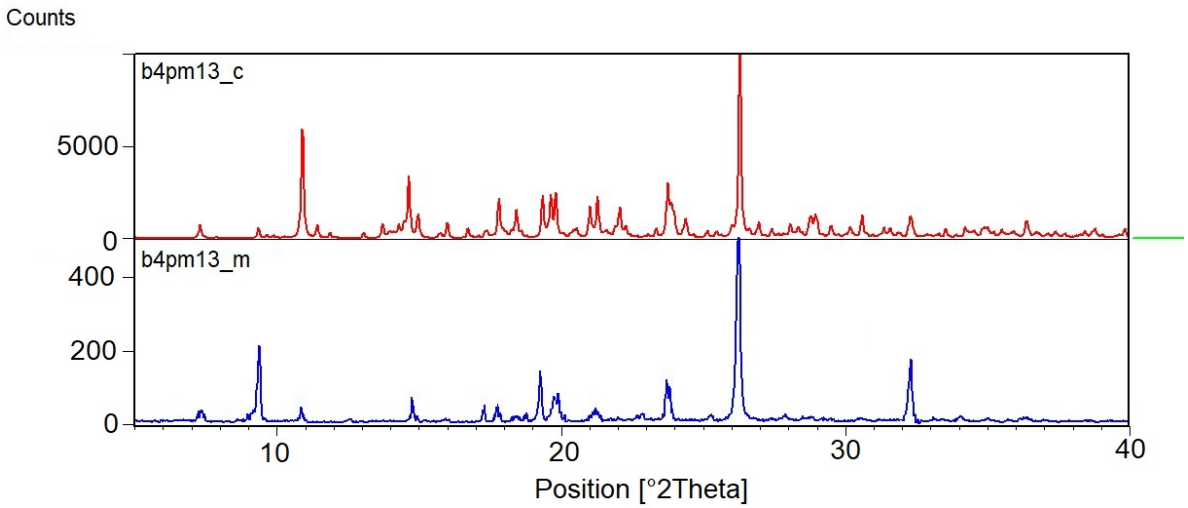

Figure S8. Measured (blue) and calculated (red) PXRD patterns of (**b4pm**)(**13tfib**).

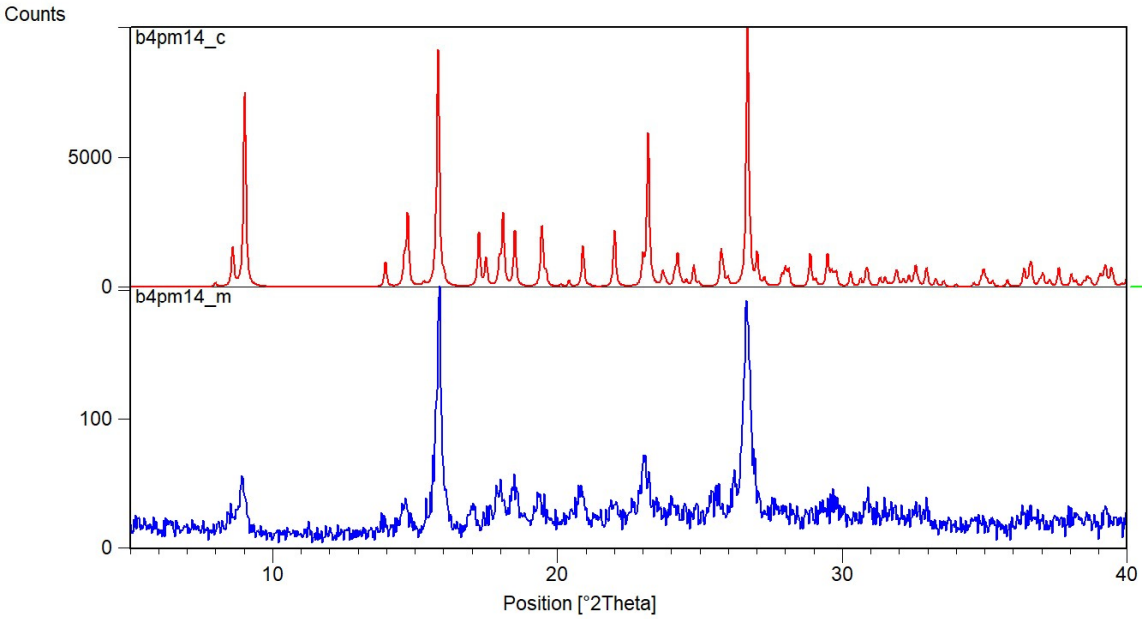

Figure S9. Measured (blue) and calculated (red) PXRD patterns of (**b4pm**)$_2$(**14tfib**).

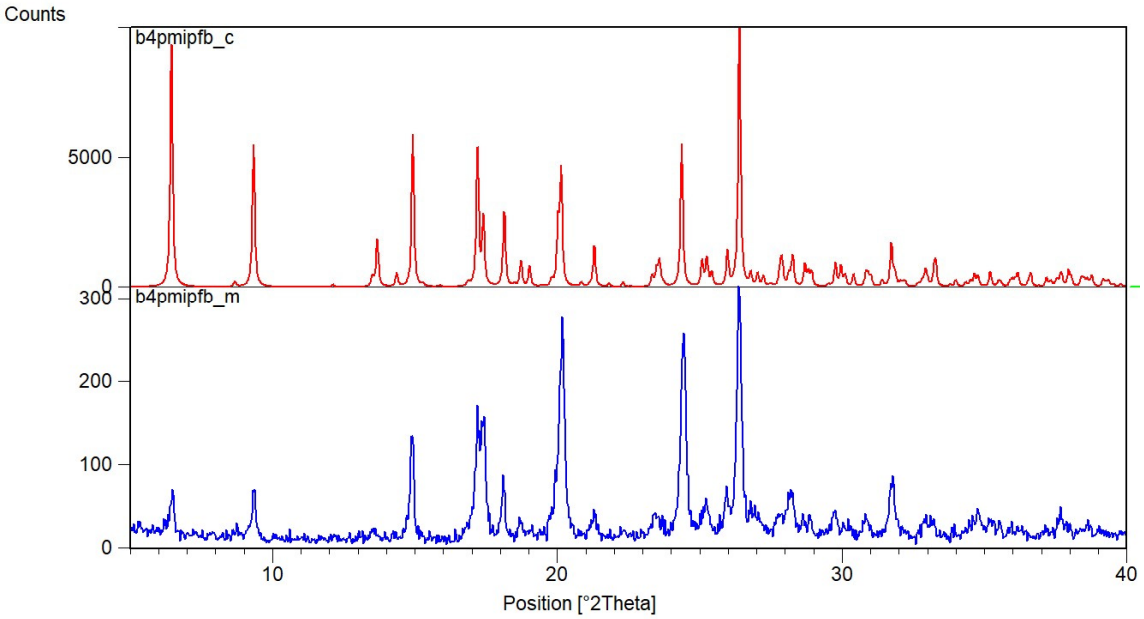

Figure S10. Measured (blue) and calculated (red) PXRD patterns of (**b4pm**)(**ipfb**).

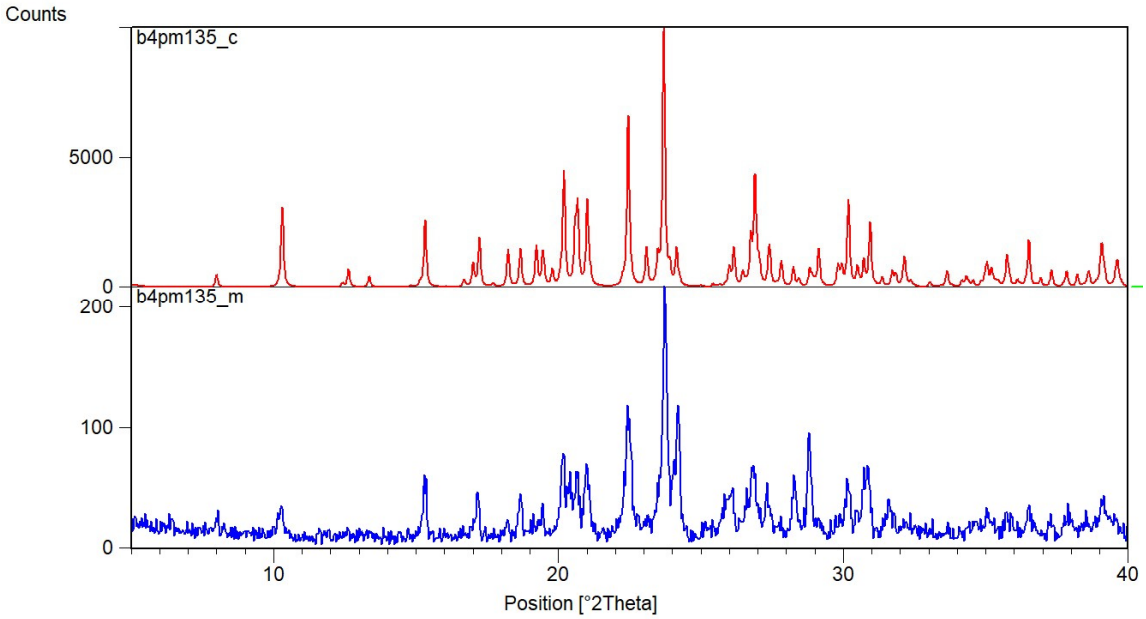

Figure S11. Measured (blue) and calculated (red) PXRD patterns of (**b4pm**)(**135tfib**).

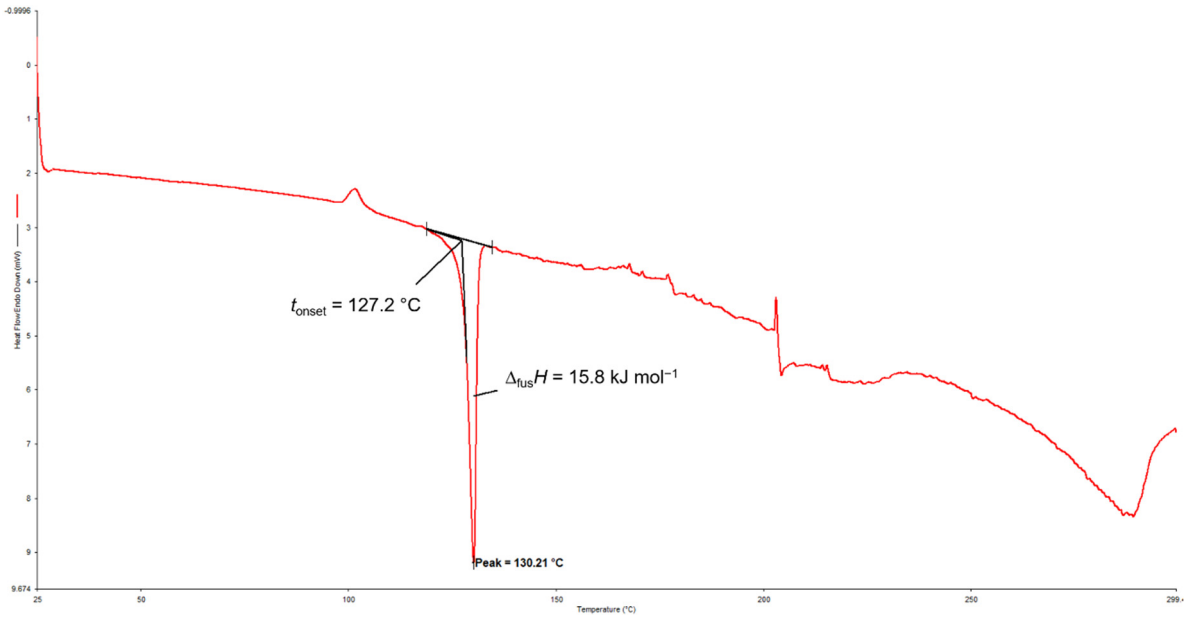

Figure S12. DSC thermogram of (**b3pm**).

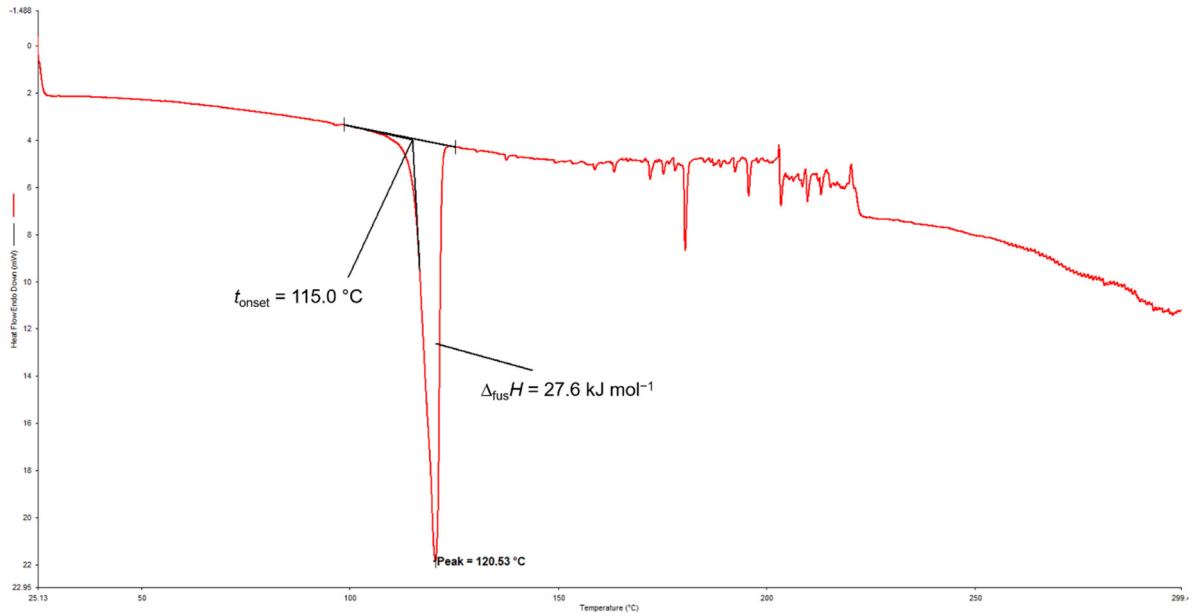

Figure S13. DSC thermogram of (**b4pm**).

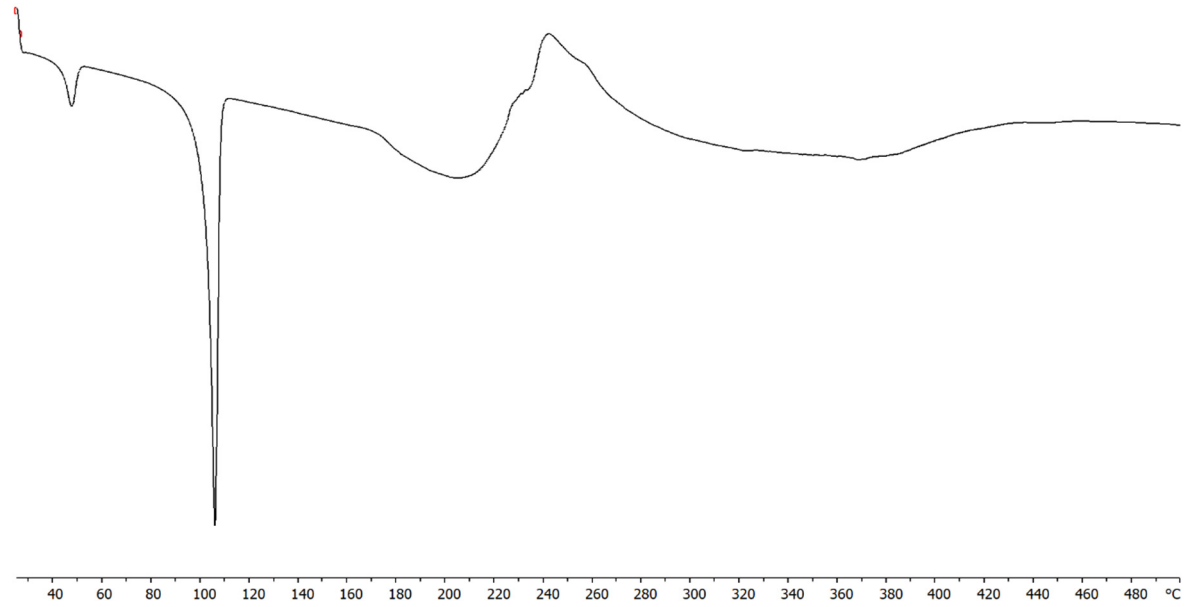

Figure S14. DSC thermogram of (**b4pm**)(**12tfib**).

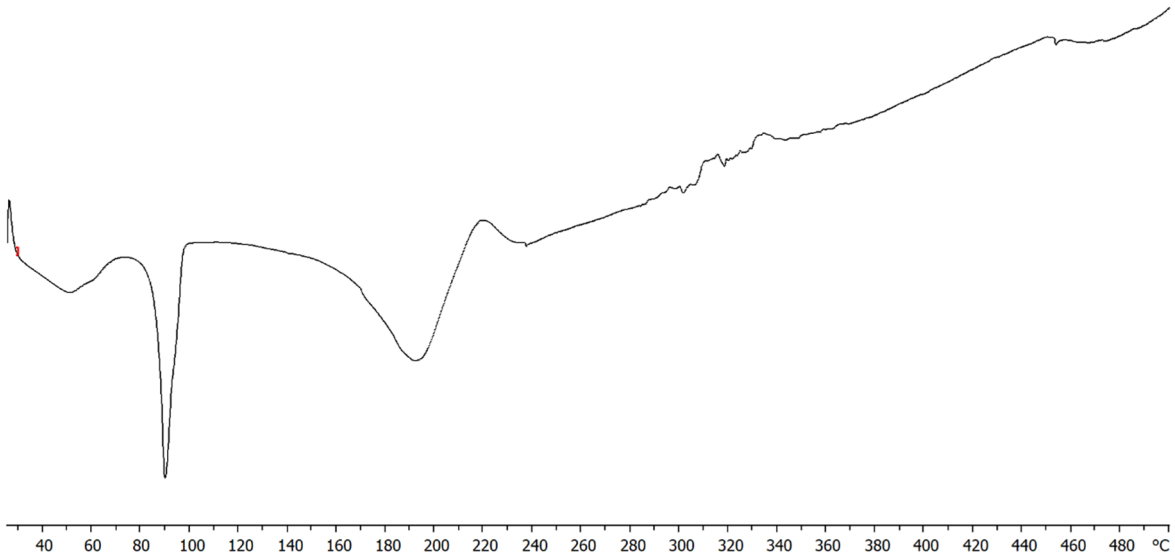

Figure S15. DSC thermogram of (**b4pm**)(**13tfib**).

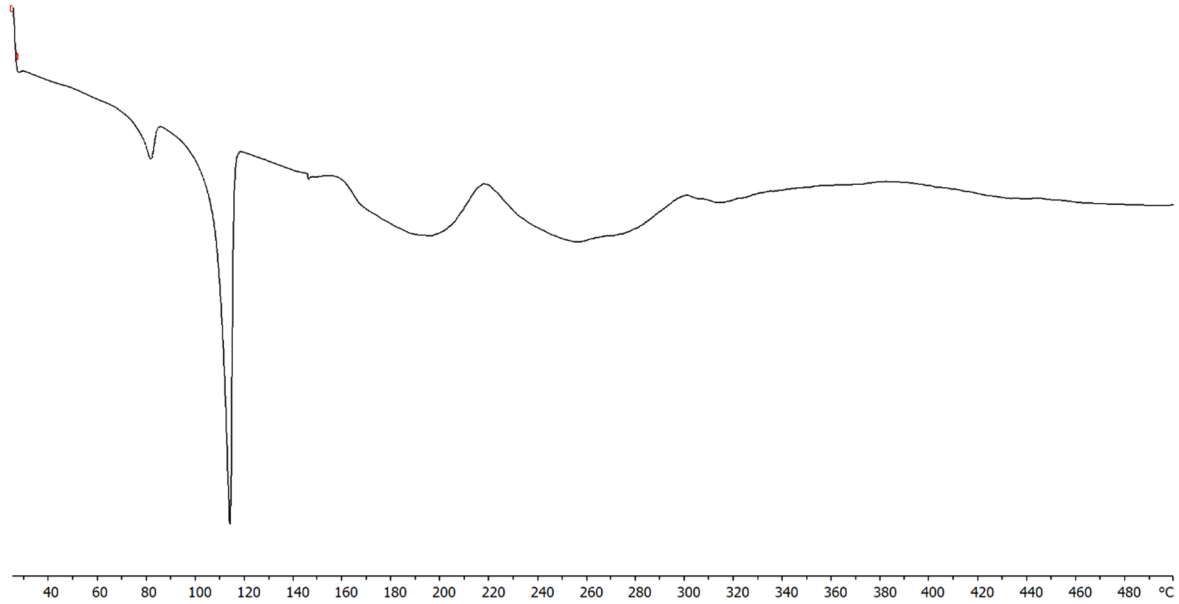

Figure S16. DSC thermogram of (**b4pm**)$_2$(**14tfib**).

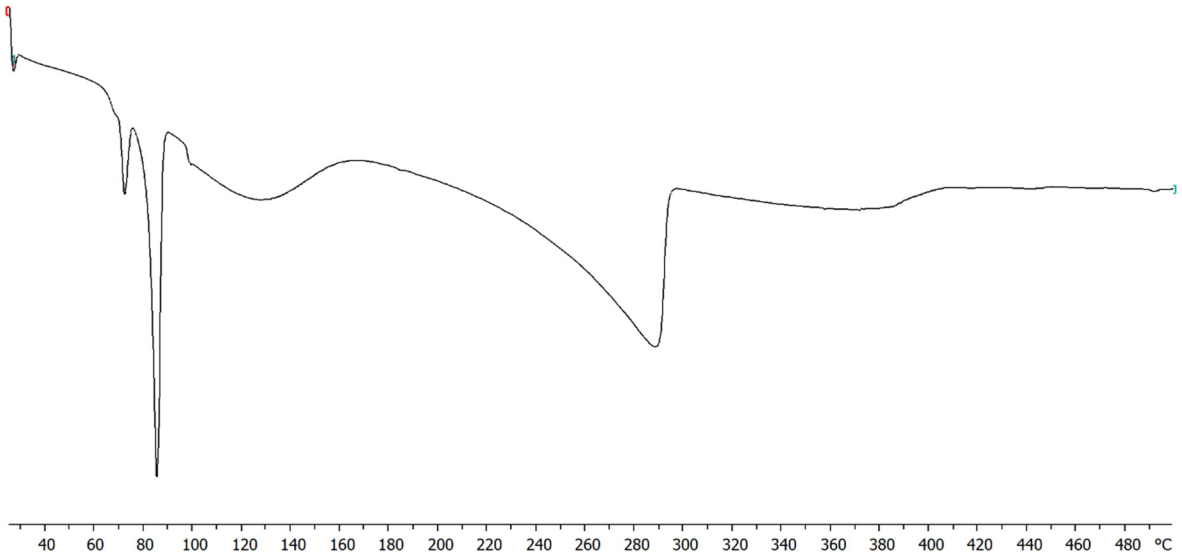

Figure S17. DSC thermogram of (**b4pm**)(**ipfb**).

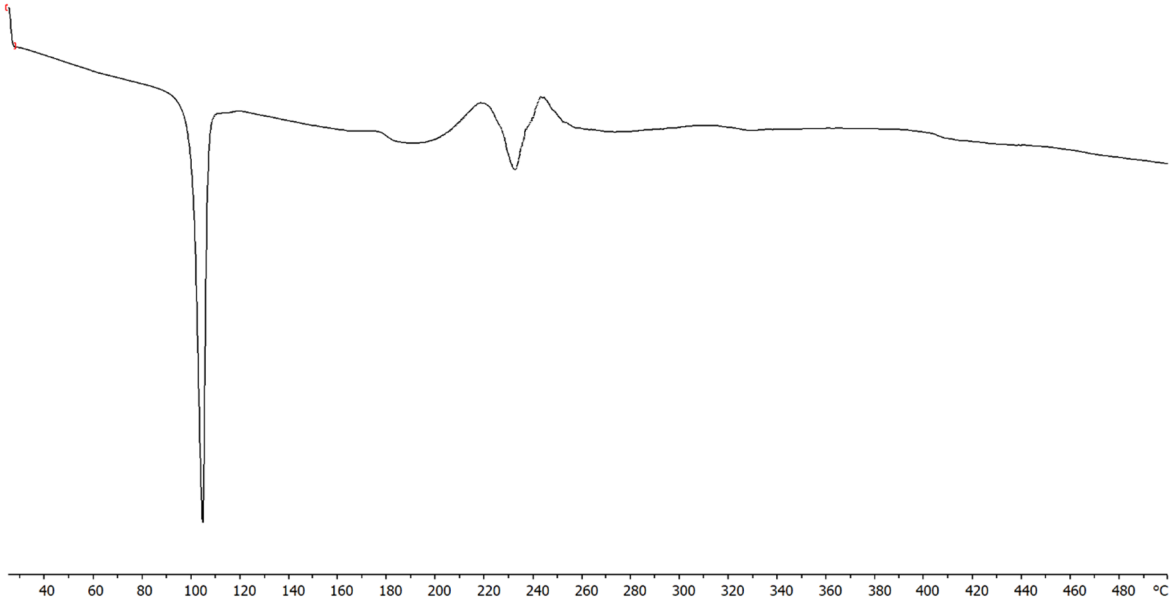

Figure S18. DSC thermogram of (**b4pm**)(**135tfib**).

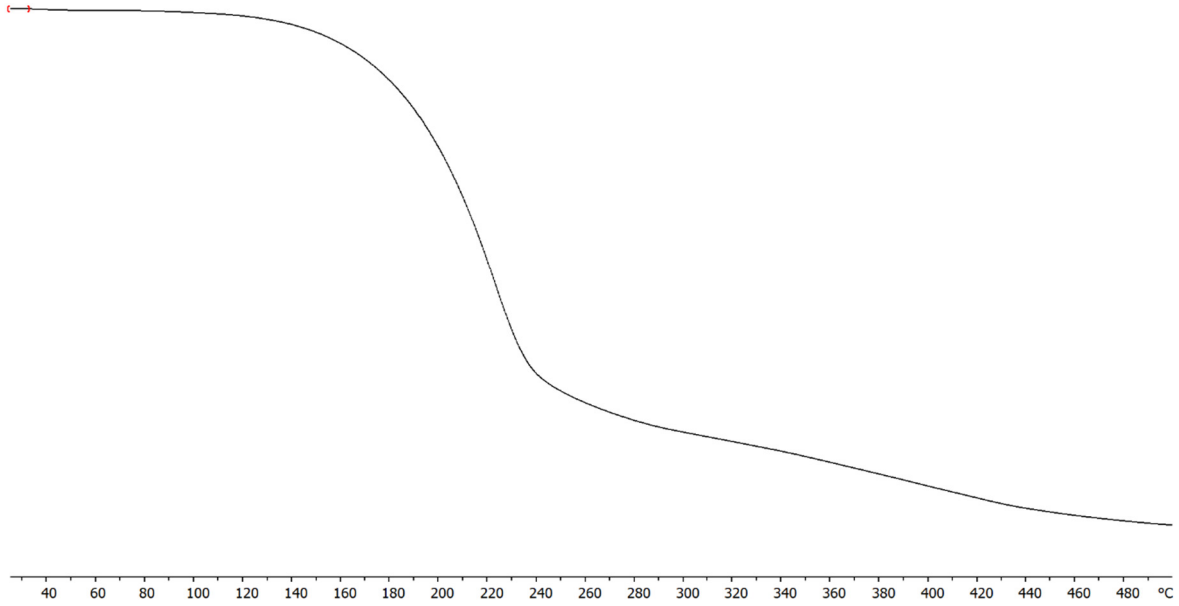

Figure S19. TG curve of (b4pm)(12tfib).

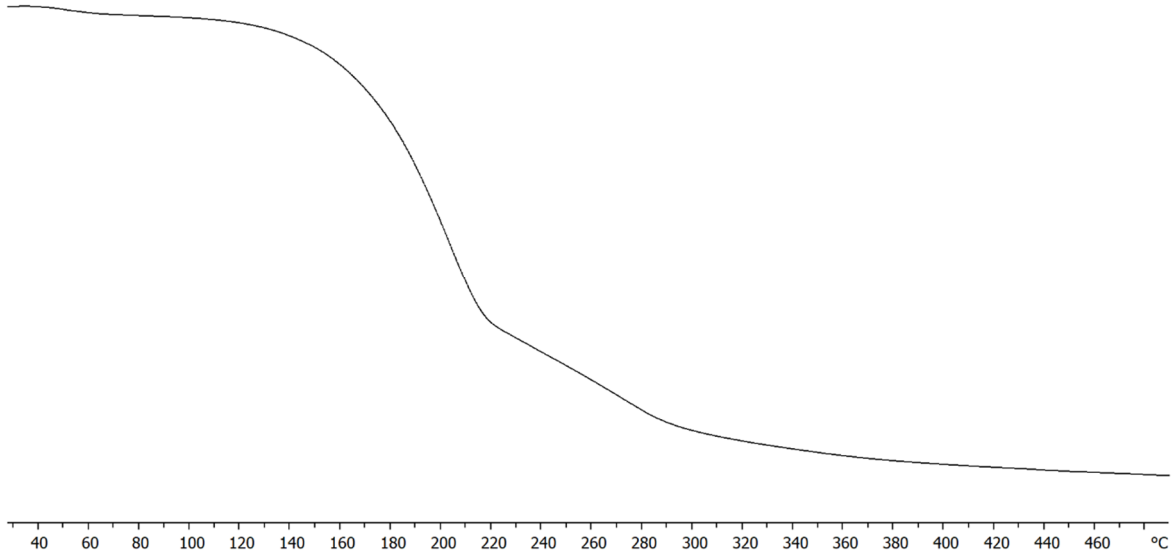

Figure S20. TG curve of (b4pm)(13tfib).

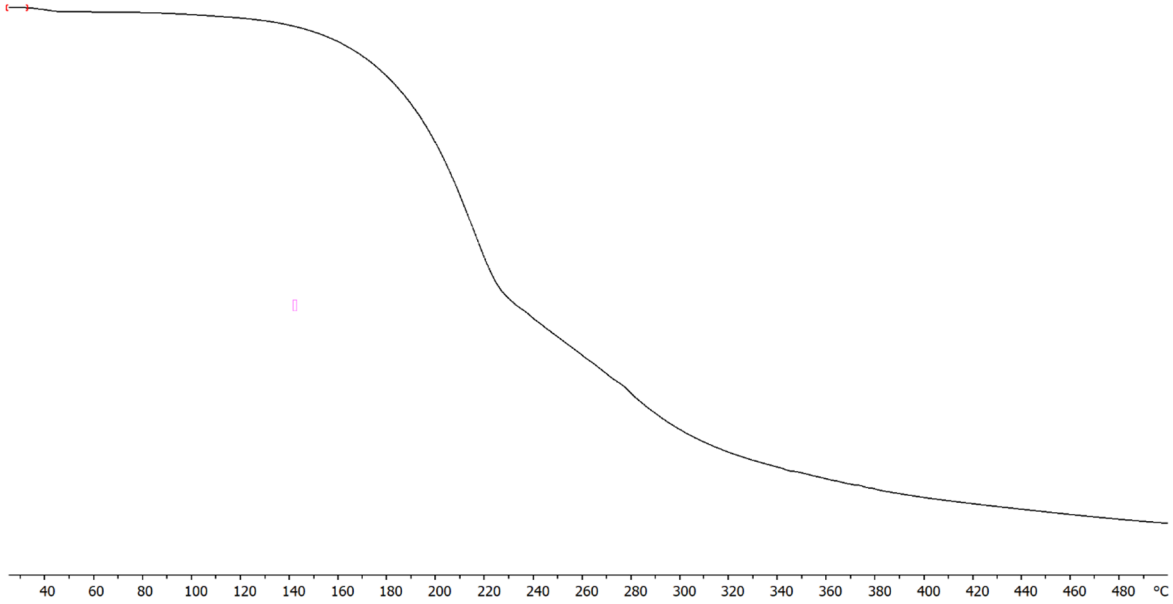

Figure S21. TG curve of $(b4pm)_2(14tfib)$.

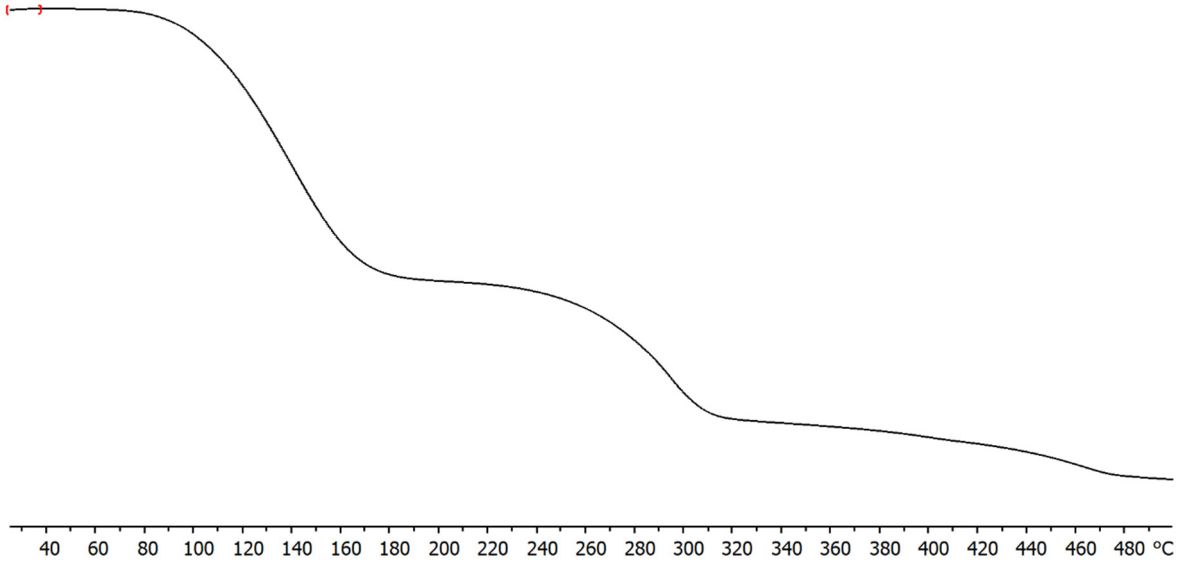

Figure S22. TG curve of (b4pm)(ipfb).

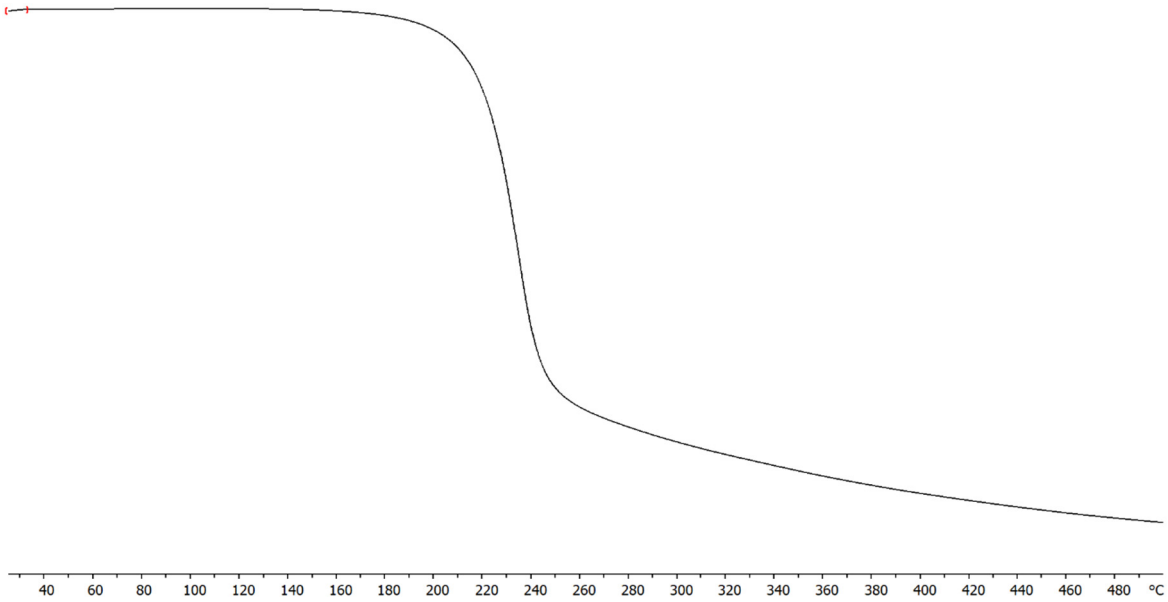

Figure S23. TG curve of (b4pm)(135tfib).

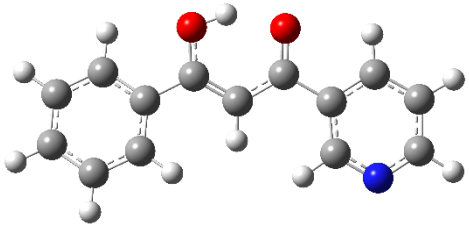

Figure S24. Optimized structure of *anti*-**b3pm**.

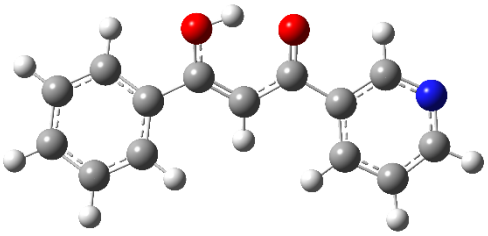

Figure S25. Optimized structure of *syn*-**b3pm**.

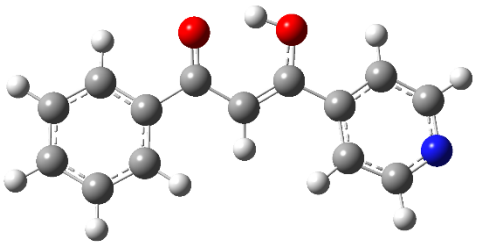

Figure S26. Optimized structure of **b4pm**.

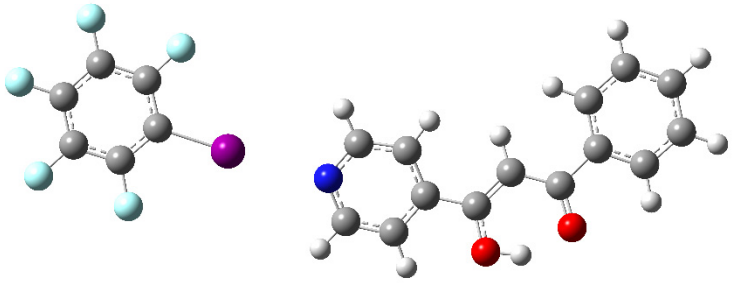

Figure S27. Optimized structure of (**b4pm**)(**ipfb**)_N.

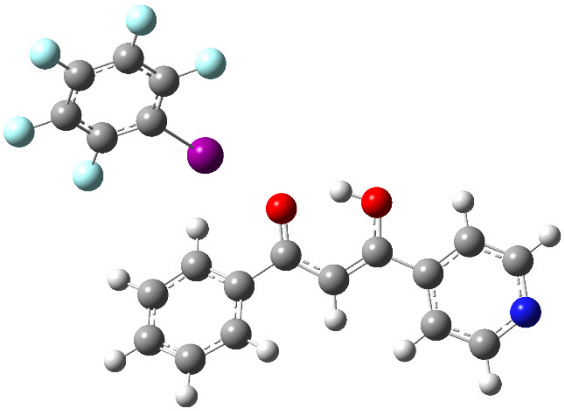

Figure S28. Optimized structure of (**b4pm**)(**ipfb**)_O.

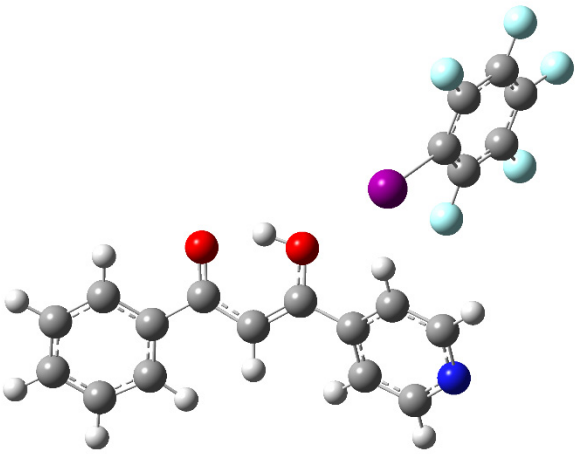

Figure S29. Optimized structure of (**b4pm**)(**ipfb**)_OH.

2. Table S1–S4

Table S1. An overview and crystallographic data of the prepared compounds.

	b3pm	**(b4pm)(12tfib)**	**(b4pm)(13tfib)**
Molecular formula	$C_{14}H_{11}NO_2$	$C_{20}H_{11}NO_2I_2F_4$	$C_{20}H_{11}NO_2I_2F_4$
M_r	225.24	627.11	627.11
Crystal system	orthorombic	triclinic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
a / Å	3.9563(6)	7.1884(3)	13.1561(12)
b / Å	16.7245(21)	7.6487(3)	13.2886(13)
c / Å	16.9608(24)	19.5677(7)	19.2683(19)

α / °	90	81.468(3)	104.524(9)
β / °	90	80.454(3)	95.406(8)
γ / °	90	78.710(4)	107.822(8)
V / Å^3	1122.25(3)	1032.94(10)	3050.58(145)
Z	4	2	2
ρ_{calc} / g cm^{-3}	1.33	2.02	2.05
T / K	295	295	295
Crystal size / mm^3	0.38 x 0.34 x 0.26	0.48 x 0.44 x 0.26	0.30 x 0.19 x 0.10
μ / mm^{-1}	0.090	3.096	3.144
F(000)	472.0	592.0	1772.0
Refl. collected/unique	11466/1973	9605 / 5907	21837 / 10573
parameters	158	267	784
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.172; –0.183	1.148; –0.951	1.304; –0.581
$R[F^2 > 4\sigma(F^2)]$	0.062	0.039	0.037
w$R(F^2)$	0.140	0.092	0.069
Goodness of fit, S	1.069	0.865	1.304

Table S2. Continuation.

	(b4pm)$_2$(14tfib)	**(b4pm)(ipfb)**	**(b4pm)(135tfib)**
Molecular formula	$C_{34}H_{22}N_2O_4I_2F_4$	$C_{20}H_{11}NO_2IF_5$	$C_{20}H_{11}NO_2I_3F_3$
M_r	852.36	519.21	735.01
Crystal system	triclinic	triclinic	monoclinic
Space group	P –1	P–1	$P2_1/c$
a / Å	6.3741(6)	6.6164(11)	22.1209(22)
b / Å	11.6659(10)	10.7159(14)	9.3223(8)
c / Å	12.4722(13)	14.4376(16)	10.6288(10)
α / °	109.136(9)	73.350(11)	90
β / °	103.357(8)	80.309(12)	92.355(9)
γ / °	104.772(7)	80.607(13)	90
V / Å^3	795.40(53)	959.53(39)	2190.00(9)
Z	2	2	4
ρ_{calc} / g cm^{-3}	1.78	1.80	2.23
T / K	295	295	295
Crystal size / mm^3	0.38 x 0.28 x 0.20	0.29 x 0.19 x 0.19	0.30 x 0.12 x 0.10
μ / mm^{-1}	2.042	1.732	4.323
F(000)	414.0	504.0	1360.0
Refl. collected/unique	6732 / 3534	6154 / 3360	25188 / 4744
parameters	212	266	266
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.441; –0.568	0.677; –0.507	1.091; –1.218
$R[F^2 > 4\sigma(F^2)]$	0.046	0.037	0.054
w$R(F^2)$	0.090	0.072	0.129
Goodness of fit, S	0.965	0.828	1.033

Table S3. CO bond lengths and their differences both in optimized structures of **b4pm** tautomers and **b4pm** molecules present in crystal structures of cocrystals.

compound	d**(CO)$_{py}$ / Å**	d**(CO)$_{bz}$ / Å**	d**(CO)$_{py}$ − d(CO)$_{bz}$ / Å**
b4pm_formI$_{calc}$	1.246	1.326	−0.080
b4pm_formII$_{calc}$	1.328	1.245	0.083
(**b4pm**)(**ipfb**)	1.300	1.270	0.030
(**b4pm**)(**12tfib**)	1.311	1.269	0.042

	1.269	1.289	−0.020
(**b4pm**)(**13tfib**)	1.294	1.287	0.007
	1.313	1.245	0.068
(**b4pm**)$_2$(**14tfib**)	1.294	1.264	0.030
(**b4pm**)(**135titfb**)	1.307	1.273	0.034

Table S4. Molar fraction of **b4pm** form I and form II molecules in cocrystals, calculated with respect to data represented in Table S3.

compound	x_I(py)	x_I(bz)	x_{II}(py)	x_{II}(bz)	<x_{II}>	σx_{II}
(**b4pm**)(**ipfb**)	0.34	0.31	0.66	0.69	0.68	0.02
(**b4pm**)(**12tfib**)	0.21	0.29	0.79	0.71	0.75	0.06
	0.72	0.54	0.28	0.46	0.37	0.13
(**b4pm**)(**13tfib**)	0.41	0.52	0.59	0.48	0.54	0.07
	0.18	0.00	0.82	1.00	0.91	0.13
(**b4pm**)(**14tfib**)	0.41	0.23	0.59	0.77	0.68	0.13
(**b4pm**)(**135titfb**)	0.25	0.34	0.75	0.66	0.70	0.06

Total Electron Energies and Cartesian Coordinates for Optimised Structures

anti-**b3pm**

E = −745.060197200 a.u.

atom	*x*	*y*	*z*
C	2.672005	1.290418	-0.01462
C	2.552336	-0.10304	0.004369
C	3.726405	-0.85825	0.080262
C	4.945168	-0.1979	0.143243
H	1.794553	1.927429	-0.08982
H	3.652993	-1.94134	0.086641
H	5.880653	-0.74338	0.205915
C	1.246254	-0.8276	-0.07024
C	0.00177	-0.09923	-0.00296
C	-1.19824	-0.76095	-0.09149
C	-2.5155	-0.09061	-0.0297
C	-2.65371	1.281643	-0.27448
C	-3.65031	-0.8532	0.272825
C	-3.90587	1.883521	-0.20277
H	-1.79121	1.879736	-0.5505
C	-4.90106	-0.24663	0.35022
H	-3.53881	-1.91765	0.448502
C	-5.03182	1.121753	0.114687
H	-4.00558	2.945585	-0.40239
H	-5.77488	-0.84249	0.593669
H	-6.00802	1.59314	0.172098
O	1.273637	-2.0698	-0.18514
O	-1.27547	-2.07897	-0.22377
H	-0.00205	0.967077	0.165162
H	-0.33774	-2.42722	-0.23315
C	4.945998	1.198344	0.122605
H	5.882647	1.748913	0.170828
N	3.837351	1.938663	0.04181

syn-**b3pm**

$E = -745.587770$ a.u.

atom	*x*	*y*	*z*
C	2.666541	1.289022	0.207238
C	2.542057	0.087979	0.016850
C	3.704140	0.820284	0.261195
H	1.805456	1.902662	0.453498
H	3.627403	1.895154	0.403251
C	1.246248	0.824687	0.114727
C	0.000983	0.097181	0.021920
C	-1.199392	0.754031	0.131323
C	-2.516140	0.086887	0.033020
C	-2.655012	1.294093	0.221443
C	-3.648783	0.859574	0.250719
C	-3.904990	1.894697	0.110962
H	-1.794030	1.900707	0.483388
C	-4.897569	0.254649	0.366704
H	-3.537290	1.930393	0.382504
C	-5.028583	1.122249	0.188639
H	-4.005286	2.964115	0.266472
H	-5.769683	0.858580	0.595984
H	-6.003175	1.592162	0.276666
O	1.277198	2.062149	0.261127
O	-1.277035	2.065650	0.316656
H	0.002678	0.959132	0.204544
H	-0.340551	2.416313	0.333583
C	5.014363	1.043485	0.183590
H	6.013447	1.464098	0.270778
C	3.927662	1.866797	0.108750
H	4.072867	2.931059	0.258973
N	4.916816	0.277361	0.368110

b4pm

$E = -745.058555310$ a.u.

atom	*x*	*y*	*z*
C	3.94284	1.84766	-0.0944
C	2.67394	1.2769	-0.1949
C	2.54523	-0.1007	-0.0157
C	3.69905	-0.8384	0.25051
C	4.91575	-0.1678	0.34149
H	4.07326	2.9176	-0.2385
H	1.82433	1.90743	-0.4339
H	3.63237	-1.9133	0.3796
H	5.8297	-0.7159	0.55684
C	1.23855	-0.8325	-0.1169
C	-0.0011	-0.1005	-0.0311
C	-1.2043	-0.7563	-0.1312
C	-2.5197	-0.0877	-0.0331
C	-2.657	1.2934	-0.2224
C	-3.6529	-0.8594	0.25158
C	-3.9066	1.89479	-0.113
H	-1.7956	1.89954	-0.4839

C	-4.9011	-0.2535	0.36689
H	-3.5424	-1.9302	0.3847
C	-5.0307	1.12335	0.1871
H	-4.0061	2.96412	-0.2693
H	-5.7737	-0.8564	0.59691
H	-6.005	1.5941	0.27453
N	5.05015	1.15239	0.17421
O	1.27107	-2.0698	-0.258
O	-1.2834	-2.0686	-0.306
H	0.00632	0.95822	0.18265
H	-0.3481	-2.4214	-0.3262

ipfb

E = −7647.918079770 a.u.

atom	*x*	*y*	*z*
C	0.212692	0.000013	0.000000
C	-0.501983	-1.194340	-0.000020
C	-1.891046	-1.202415	-0.000076
C	-2.585866	0.000012	-0.000114
C	-1.891093	1.202421	-0.000075
C	-0.501989	1.194308	-0.000017
F	0.133111	-2.363949	0.000010
F	-2.557243	-2.353703	-0.000098
F	-3.913461	-0.000051	-0.000165
F	-2.557199	2.353745	-0.000093
F	0.133058	2.363963	0.000012
I	2.298327	-0.000001	0.000091

(b4pm)(ipfb)_N

E = −8392.97279020 a.u.

atom	*x*	*y*	*z*
I	-2.569597	0.349763	0.069539
F	-4.127716	2.462054	0.013528
F	-5.264577	2.128369	0.048212
F	-8.623655	1.138885	0.076610
F	-6.739415	3.097119	0.075963
F	-7.871132	1.473005	0.014365
C	-6.946660	0.513989	0.014204
C	-6.369131	1.817903	0.045514
C	-7.333397	0.819159	0.045903
C	-5.023908	1.473428	0.013128
C	-4.610186	0.145364	0.018901
C	-5.595575	0.836727	0.017620
O	4.947851	2.613575	0.265031
H	5.948707	2.627858	0.274863
O	7.335517	1.738179	0.211338
N	0.330674	0.890604	0.082416
C	7.891497	0.545578	0.001681
C	7.517169	1.894232	0.015977
H	6.473898	2.185537	0.040284
C	0.922822	2.069219	0.296336
H	0.263496	2.901767	0.528694

C	3.114164	1.160665	0.063516
C	2.498509	0.071597	0.296696
H	3.069447	0.952918	0.567271
C	5.478808	0.313557	0.034272
H	5.105414	0.686429	0.128071
C	2.300697	2.256837	0.230039
H	2.737784	3.233700	0.401653
C	9.838098	2.547077	0.154937
H	10.592902	3.324852	0.217935
C	9.249844	0.208726	0.055549
H	9.522187	0.841424	0.035310
C	6.907935	0.574944	0.091474
C	4.585861	1.343667	0.128768
C	10.217706	1.203390	0.135554
H	11.268239	0.934649	0.182070
C	8.488089	2.890623	0.092574
H	8.190625	3.934280	0.102425
C	1.112621	0.153368	0.212256
H	0.602936	1.096564	0.395437

(b4pm)(ipfb)_O

E = −8392.95640280 a.u.

atom	x	y	z
53	-1.151168	0.307271	0.563307
9	-3.544180	1.780708	0.109937
9	-2.963939	-2.912587	0.006286
9	-5.560390	-3.206609	0.636375
9	-7.160310	-1.026286	0.898284
6	-4.010551	0.544658	0.069171
6	-5.352618	0.396994	0.395622
6	-3.717800	-1.819925	0.125860
6	-3.170099	-0.555732	0.071857
6	-5.057853	-1.987397	0.451765
6	-5.876832	-0.874514	0.587026
8	3.643237	-1.592246	0.912805
1	2.754863	-1.210955	1.166583
6	4.314897	-0.648165	0.271956
8	1.733066	0.089203	1.105665
6	5.675282	-1.057173	0.136740
6	6.464080	-0.264262	0.981577
1	6.085255	0.673715	1.373137
6	3.770639	0.594506	0.031898
1	4.365132	1.361730	0.442264
6	2.441426	0.907020	0.471863
6	1.867577	2.258149	0.185801
6	2.233004	3.013409	0.929037
1	2.959134	2.649729	1.649271
6	1.608510	4.243750	1.132048
1	1.861841	4.848185	1.999534
6	6.181188	-2.277505	0.329809
1	5.565942	-2.892094	0.977130

6	0.345922	4.020240	0.755436
1	-0.408699	4.450056	1.409188
6	0.896857	2.774219	1.044374
1	0.586837	2.213738	1.920095
6	7.739018	-0.682638	1.346210
1	8.341552	-0.064390	2.003590
6	7.458545	-2.692256	0.035525
1	7.843630	-3.637682	0.332526
9	-6.137702	1.464803	0.524768
6	8.240082	-1.896788	0.872766
1	9.235249	-2.221521	1.159836
7	0.685970	4.751340	0.310971

(b4pm)(ipfb)_OH

E = −8392.93993320 a.u.

atom	x	y	z
I	1.111892	0.184696	0.626435
F	2.572377	0.016439	2.229177
F	3.754401	1.081785	2.216579
F	6.291244	1.493220	1.429454
F	6.985581	1.158801	1.176766
C	3.463221	0.353434	1.309952
C	4.772955	0.566585	1.720590
C	4.058692	0.907332	0.931405
C	3.082776	0.518195	0.018719
C	5.373283	1.124397	0.538528
C	5.730259	0.953101	0.792281
O	-3.659444	1.461242	1.272492
C	-4.229371	0.713732	0.454561
C	-5.519587	1.184337	0.147391
C	-6.120487	0.586722	1.255493
H	-5.678201	0.264530	1.761750
C	-3.687860	0.576963	0.098536
H	-4.239133	1.249888	0.542553
C	-2.501996	0.999857	0.641723
C	-1.873306	2.303006	0.350451
C	-2.108312	2.970743	0.857593
H	-2.742709	2.519905	1.614727
C	-1.491759	4.192001	1.110858
H	-1.665885	4.698430	2.054646
C	-6.145308	2.294173	0.421061
H	-5.695014	2.786138	1.276430
C	-0.398983	4.091366	1.042910
H	0.267232	4.525325	1.781425
C	-1.008139	2.866222	1.297090
H	-0.826169	2.343134	2.230451
C	-7.314428	1.124001	1.737270
H	-7.800653	0.682706	2.603960
C	-7.340265	2.744837	0.132904
H	-7.852965	3.603534	0.293470
F	5.114519	0.401645	2.996818

O	-1.813944	0.255001	1.507449
H	-2.348157	0.583448	1.659463
N	-7.925758	2.178917	1.193938
C	-0.639207	4.755599	0.159947
H	-0.157415	5.707454	0.360280

(*anti*-b3pm)(ipfb)_N

E = −8392.9907770 a.u.

atom	x	y	z
C	1.756905	1.989122	0.020614
C	3.021678	2.579204	0.072835
C	3.096925	3.972956	0.004760
C	1.926093	4.705720	-0.134802
H	1.631862	0.911726	0.103565
H	4.071680	4.447366	0.064747
H	1.940782	5.788212	-0.198151
C	4.292077	1.802657	0.227150
C	4.298897	0.377698	0.013967
C	5.458906	0.343456	0.171289
C	5.558609	1.803664	-0.037004
C	4.422402	2.623450	-0.054002
C	6.824113	2.376450	-0.215160
C	4.550328	3.992856	-0.261536
H	3.437536	2.202316	0.120540
C	6.947973	3.746472	-0.427987
H	7.700821	1.738614	-0.189769
C	5.812902	4.556738	-0.453321
H	3.666018	4.621703	-0.265350
H	7.931087	4.182993	-0.572049
H	5.910836	5.625635	-0.615311
O	5.324096	2.435031	0.528608
O	6.605753	0.228516	0.510830
H	3.408395	0.128010	-0.329002
H	6.432567	1.209639	0.598010
C	0.714148	4.017816	-0.188329
H	0.226292	4.552644	-0.297529
N	0.624983	2.686832	-0.105185
C	5.952284	0.458633	-0.118279
C	5.806196	1.821901	0.100520
C	4.538132	2.362019	0.269196
C	3.425897	1.531393	0.218316
C	3.545340	0.162402	0.001123
C	4.826426	0.354113	-0.166030
I	1.852325	1.079088	-0.064519
F	2.224812	2.088106	0.386051
F	4.396310	3.670131	0.477418
F	6.877121	2.608147	0.147585
F	7.167992	0.059829	-0.281870
F	5.008414	1.657967	-0.377996

(*syn*-b3pm)(ipfb)

E = −8392.987287660 a.u.

atom	*x*	*y*	*z*
C	-5.076389	2.228301	0.192224
C	-2.778406	0.865531	-0.144772
C	-1.436598	0.485384	-0.270546
H	-4.094345	2.587564	-0.082143
H	-1.176467	0.569226	-0.228652
C	-3.796551	0.214278	0.052767
C	-5.203691	0.099679	0.009061
C	-6.140962	0.884727	0.213120
C	-7.600764	0.649802	0.184404
C	-8.143384	0.626926	0.379417
C	-8.456163	1.736566	-0.033280
C	-9.521390	0.814700	0.342469
H	-7.494921	1.470923	0.592854
C	-9.834061	1.543831	-0.077262
H	-8.030364	2.724613	-0.169926
C	10.369250	0.269322	0.109016
H	-9.935838	1.804532	0.504461
H	10.491519	2.388857	-0.254744
H	11.444137	0.120710	0.080217
O	-3.385832	1.374798	0.248358
O	-5.807612	2.147834	0.436703
H	-5.540848	1.095602	-0.237308
H	-4.808847	2.198877	0.413298
C	-0.740645	2.656468	-0.483528
H	0.097606	3.336989	-0.615056
C	6.116699	1.818050	-0.085920
C	7.080285	0.881193	0.261918
C	6.714169	0.442366	0.466175
C	5.384501	0.817155	0.321679
C	4.399945	0.102172	-0.026057
C	4.792511	1.422199	-0.226179
I	2.393041	0.481473	-0.236952
F	5.073789	2.097987	0.528470
F	7.638407	1.342783	0.798456
F	8.350640	1.250140	0.398461
F	6.467080	3.087918	-0.283325
F	3.897097	2.352234	-0.560673
N	-0.438814	1.353568	-0.438387
C	-2.040600	3.141045	-0.364891
H	-2.230917	4.207885	-0.401045