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The combination of halogen and hydrogen bonding: a versatile tool in coordination chemistry

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Supporting Information

Table S1. Distances and angles of hydrogen bonds in **INPBA** and crystal structures **1** to **4**

Crystal	D−H (Å)	D···A (Å)	< DHA (deg)
INPBA			
N(1)−H···O(1)	0.860	3.151(9)	152.6
C(12)−H···O(1)	0.930	3.276(2)	132.7
[Ag(**INPBA**)$_2$]NO_3			
N(2)−H···O(5)	0.860(3)	3.024(4)	158.8(2)
N(4)−H···O(4)	0.860(3)	2.958(4)	161.5(2)
C(24)−H···O(4)	0.930(4)	3.385(5)	162.8(3)
C(16)−H···O(5)	0.930(5)	3.441(6)	143.6(3)
C(2)−H···O(5)	0.930(4)	3.275(8)	136.9(2)
C(8)−H···O(5)	0.930(4)	3.268(4)	156.6(3)
C(8)−H···O(1)	0.929(4)	3.517(5)	172.6(3)
C(23)−H···O(3)	0.929(4)	3.430(5)	159.2(3)
[$ZnBr_2$(**INPBA**)$_2$]			
N(4)−H···O(2)	0.860	2.795(6)	149.2
C(14)−H···O(2)	0.929	3.077(8)	117.3
C(20)−H···O(2)	0.930	3.368(7)	158.6
C(5)−H···O(1)	0.930	3.577(8)	158.1
N(2)−H···Br(1)	0.860	3.743(5)	150.9
C(8)−H···Br(1)	0.931	3.710(6)	153.6
[$Zn(OCOPh)_2$(**INPBA**)$_2$]			
N(2)−H···O(2)	0.83(3)	2.822(3)	167(3)
C(9)−H···O(2)	0.94(3)	3.149(3)	138(3)
C(15)−H···O(2)	0.91(4)	3.274(2)	130(3)
[Hg_2I_2(**INPBA**)]$_n$			
C(9)−H···O(1)	0.93(1)	2.616(2)	168.9(7)

Table S2 Geometrical parameters and uncorrected and corrected interaction energies of optimized dimers (ΔE and ΔE_{BSSE}, respectively)

Dimer	ΔE	ΔE_{BSSE}	*d(I···N)*	*<(C-I···N)*	*d(O···H)*	*<(C-O···H)*	*Reduction sum vderW radii*
	kcal/mol	kcal/mol	Å	deg	Å	deg	%
XB-exp			2.989	175.3			15
HB-exp					2.366	157.6	13
XB-opt	-8.5	-6.6	2.911	178.8			18
HB-opt	-21.0	-16.6			1.890	136.3	33

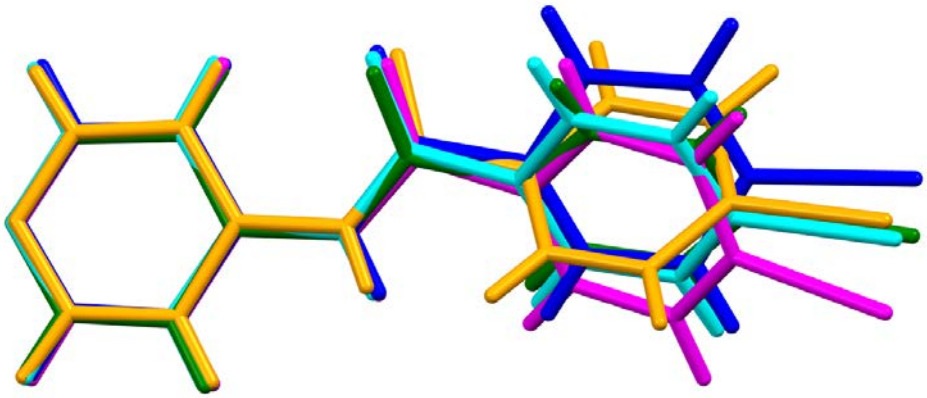

Figure S1. Superposition of INPBA ligand in crystal structures **INPBA** (green), **1** (blue), **2** (magenta), **3** (orange) and **4** (cyan).

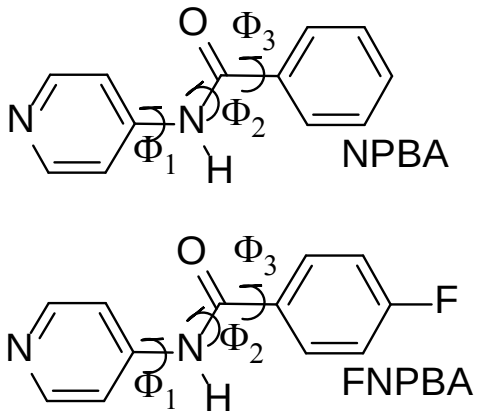

Figure S2. N-(4-pyridyl)benzamide (NPBA) and 4-fluoro-N-(pyridine-4-yl)benzamide (FNPBA).

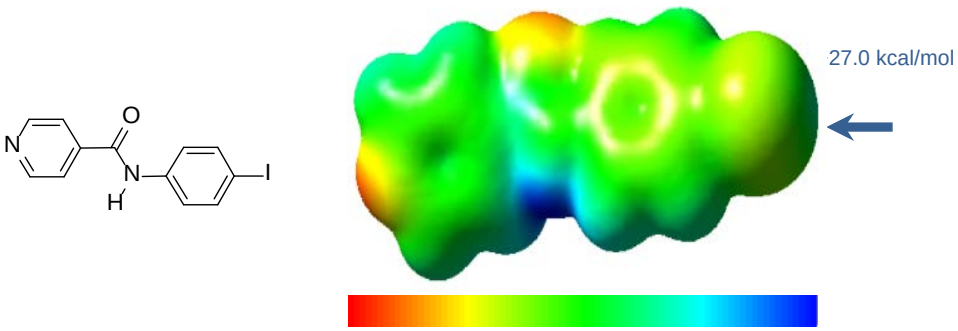

Figure S3. Computed electrostatic potential of the optimized N-(4-iodophenyl)isonicotinamide obtained by molecular electron density 0.002 electron/Å. Electrostatic values range from –51.4 (red) to 67.1 (blue) kcal/mol.

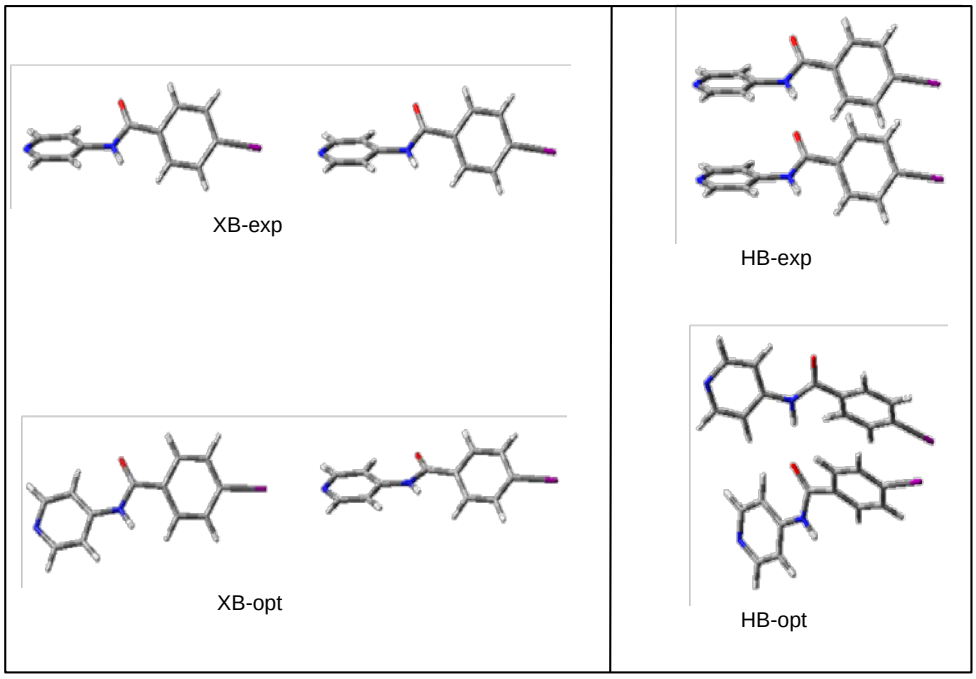

Figure S4. Extracted dimers from **INPBA** crystal structure, XB-exp and HB-exp, and these dimers after optimization, XB-opt and HB-opt, using B3LYP-D3/6-311G^{++}(d,p) and DGDZVP.

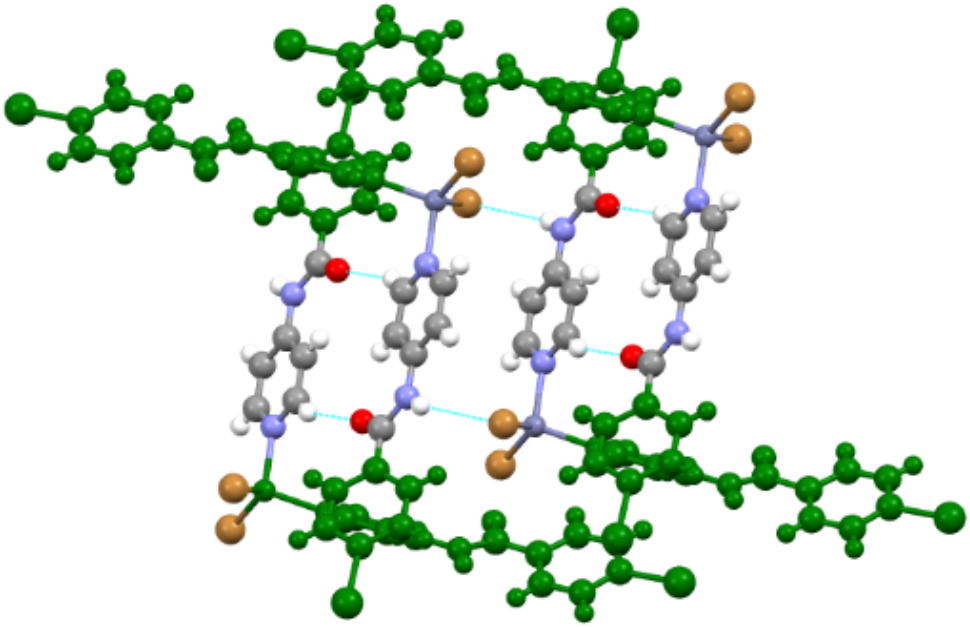

Figure S5. A view of the ladder structure formed by amide hydrogen bonds in **2**.

Calculated gas-phase energy of INPBA and dimers optimized with B3LYP-D3/6-311G++(d,p)-DGDZVP and Cartesian coordinates of calculated structures.

INPBA; Energy (E_{au}), -7567.32405 Hartrees

I	-4.48147700	-0.26322400	-0.02081900
O	2.25766700	1.99623800	0.19660700
N	2.68979000	-0.25771400	-0.09692300
H	2.25535300	-1.13870900	-0.31975800
C	-2.37335100	0.07468000	0.01691800
N	6.90653900	-0.48537600	-0.01566600
C	-1.51520700	-0.96271200	0.38939000
H	-1.91048400	-1.92570500	0.67297000
C	-0.13841500	-0.73980500	0.40642700
H	0.50805300	-1.54117500	0.73906900
C	0.38707100	0.51166200	0.05277400
C	-0.49156100	1.54694100	-0.29405600
H	-0.07797400	2.51501000	-0.53423600
C	-1.86716400	1.33372400	-0.32085000
H	-2.53378700	2.13562500	-0.59737800
C	1.84572200	0.82371000	0.06664700
C	4.09743900	-0.27780600	-0.06505700
C	4.89210200	0.85385300	0.17226000
H	4.43750200	1.81494600	0.32940100
C	6.27661800	0.69281100	0.18696600
H	6.91868300	1.54308600	0.36709100
C	6.12682600	-1.56598600	-0.24540100
H	6.64603500	-2.50015700	-0.40616300
C	4.73915900	-1.50981100	-0.27754000
H	4.16383700	-2.40791200	-0.46315800

HB-opt; Energy (E_{au}), -15134.68158 Hartrees

I	3.74827400	-0.58254600	-2.15744400
O	-1.29539700	4.22595100	-0.66126000
N	-2.52671200	2.28070800	-0.36474300
H	-2.46046700	1.26716700	-0.29481200
C	2.03268200	0.61469500	-1.72448700
N	-6.35040200	3.71156200	0.72830600
C	0.76285600	0.12192400	-2.02977800
H	0.64756200	-0.84125600	-2.50201600
C	-0.36103800	0.88587800	-1.71921500
H	-1.33974200	0.49747500	-1.95721300
C	-0.22218800	2.13634800	-1.10449800
C	1.06170200	2.63614000	-0.84999000
H	1.15544000	3.61901500	-0.41207400
C	2.19190600	1.87724900	-1.14511300
H	3.17638900	2.25821000	-0.92313600
C	-1.39034600	2.97761900	-0.70845400
C	-3.77944400	2.81229100	-0.00279000
C	-4.09286300	4.18024800	-0.02755500
H	-3.35079000	4.90278200	-0.31479200
C	-5.37952400	4.56871000	0.34220700
H	-5.65352400	5.61431400	0.33267100
C	-6.03047200	2.39679800	0.75087300
H	-6.81713600	1.72464200	1.06451400
C	-4.77899600	1.90727100	0.39971100
H	-4.56890700	0.84849400	0.43993700
I	4.13376600	0.15232000	2.13883700
O	-2.60852300	-0.57459500	0.10362300

N	-2.23228100	-2.78746200	0.63248700
H	-1.59205100	-3.40550000	1.10678200
C	2.14344000	-0.44028400	1.66500800
N	-5.79589700	-4.72173400	-0.55094700
C	1.90586100	-1.70116900	1.11173600
H	2.72336000	-2.37715800	0.91965400
C	0.60335600	-2.06389500	0.77293100
H	0.43759700	-3.01882900	0.29196000
C	-0.45997100	-1.17210800	0.97812500
C	-0.20258300	0.08891000	1.53206700
H	-1.01699800	0.78272200	1.67492400
C	1.09209500	0.45501500	1.88230300
H	1.28111000	1.43053500	2.30082100
C	-1.84345600	-1.47705700	0.53895800
C	-3.44564000	-3.38219400	0.22074600
C	-4.46525700	-2.69759800	-0.45501600
H	-4.36863600	-1.65235800	-0.68269300
C	-5.60849500	-3.41080300	-0.81471700
H	-6.41474100	-2.91590000	-1.33641800
C	-4.80378800	-5.36764700	0.10197900
H	-4.97224600	-6.41544300	0.30451000
C	-3.62678200	-4.74608800	0.50114300
H	-2.86426600	-5.31081100	1.02190300

XB-opt; Energy (E_{au}), -15134.66154 Hartrees

I	11.61246200	-0.54540900	0.17622300
O	5.03845500	1.97363500	-0.82106400
N	4.45525000	-0.08878400	0.04922900
H	4.82822400	-0.90398300	0.50856700
C	9.53208200	-0.10607600	-0.01188100
N	0.24764400	-0.03215900	-0.05105300
C	8.61152300	-1.15154000	-0.11991500
H	8.94606300	-2.17725500	-0.12682700
C	7.25254400	-0.85872200	-0.23338400
H	6.55885000	-1.67966000	-0.35918900
C	6.80691100	0.47135700	-0.23981700
C	7.74770900	1.50694300	-0.15585800
H	7.39680300	2.52744600	-0.19201100
C	9.10560000	1.22553400	-0.03456100
H	9.81995400	2.03047800	0.03900100
C	5.37387900	0.85666000	-0.37484300
C	3.05296000	-0.02091700	-0.00672400
C	2.34378200	1.05987300	-0.55560400
H	2.86896000	1.90783400	-0.95525400
C	0.95309000	1.00374600	-0.55346300
H	0.37043500	1.81509500	-0.96412800
C	0.93560000	-1.06888000	0.47549500
H	0.34372700	-1.88133200	0.87085200
C	2.32212100	-1.10317000	0.51574900
H	2.82984500	-1.95588400	0.94695800
I	-2.65838400	0.13089500	0.00372600
O	-9.59059200	1.80171300	0.41750400
N	-9.82389700	-0.46834700	0.03758700
H	-9.31040000	-1.33380500	-0.00306100
C	-4.79895300	0.29550900	0.05295000
N	-14.00699800	-1.02683700	-0.13726000
C	-5.59124200	-0.64910300	-0.60924900
H	-5.12845600	-1.45348800	-1.16117600
C	-6.98107500	-0.54401800	-0.56976200
H	-7.56948600	-1.26197800	-1.12670600
C	-7.59793400	0.50451400	0.13010300

C	-6.79497700	1.46006400	0.76850700
H	-7.27811900	2.27986300	1.27937000
C	-5.40719400	1.35484400	0.73876900
H	-4.80076300	2.09201400	1.24325200
C	-9.07458200	0.68387500	0.20115000
C	-11.22315900	-0.60000900	-0.00935800
C	-12.11626400	0.47909200	0.07927700
H	-11.74709700	1.48047600	0.20604800
C	-13.48191100	0.20997600	0.00903700
H	-14.19665200	1.01799600	0.07372600
C	-13.13373900	-2.05624200	-0.21936900
H	-13.56862400	-3.03898000	-0.33559600
C	-11.75569600	-1.89212100	-0.16176000
H	-11.10274100	-2.75258900	-0.23508100