Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Interplay between non-covalent interactions in 1D supramolecular polymers based 1,4-bis(iodoethynyl)benzene

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Table S1 Crystallographic data for p-BIB, {p-BIB·DTMABr} (**1**), {p-BIB·TPABr} (**2**) and {p-BIB·TBABr} (**3**).

Compound	*p*-BIB	**1**	**2**	**3**
Empirical formula	$C_{10}H_4I_2$	$C_{23}H_{34}BrI_2N$	$C_{22}H_{32}BrI_2N$	$C_{26}H_{40}BrI_2N$
Formula weight	377.93	658.22	644.20	700.30
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a, Å	4.1533(3)	7.8843(4)	9.9332(4)	17.9505(8)
b, Å	17.1541(16)	14.5796(6)	8.8016(4)	8.6914(4)
c, Å	7.0511(5)	11.5600(4)	14.5701(7)	18.8483(7)
α, deg				
β, deg	95.332(7)	97.065(3)	98.374(4)	90.616(4)
γ, deg				
V, $Å^3$	500.19(7)	1318.73(10)	1260.25(10)	2940.4(2)
T, K	150(2)	150(2)	150(2)	150(2)
Space group	$P2_1/n$	$P2_1/m$	P2/n	P2/c
Z	2	2	2	4
μ(Mo Kα), mm^{-1}	6.229	3.908	4.087	3.510
θ range, deg	3.14 to 24.71	2.95 to 26.37	2.71 to 25.68	2.81 to 24.71
Refl. collected	1610	5627	6307	42018
Uniq reflect / R_{int}	848 / 0.0464	2803 / 0.0410	2394 / 0.0769	5007 / 0.0403
R1/wR2 (I>2σ)	0.0434 / 0.0650	0.0480 / 0.0937	0.0431 / 0.0628	0.0553 / 0.1564
R1/wR2 (all data)	0.0693 / 0.0756	0.0712 / 0.1070	0.0943 / 0.0692	0.0785 / 0.1699
Max. shift/esd	0.003	0.007	0.004	0.005
Residual ρ/e $Å^{-3}$	0.846 and –0.840	1.134 and –0.893	1.033 and –0.600	1.212 and –1.475

Table S2 Uncorrected and corrected interaction energies of the optimized trimers, (IBrI)-180, (IBrI)-139 (IBrI)-75, using B3LYP-D3 and 6-311G+(d,p)/DGDZVP or B3LYP-D3 and def2TZVP.

Complex	6-311g+(d,p)/DGDZVP		def2TZVP	
	ΔE kJ mol^{-1}	ΔE_{BSSE} kJ mol^{-1}	ΔE kJ mol^{-1}	ΔE_{BSSE} kJ mol^{-1}
(IBrI)-180	–38.7	–36.6	–40.3	–38.0
(IBrI)-139	–39.5	–37.4	–41.2	–38.9
(IBrI)-75	–39.2	–37.3	–41.1	–39.1

Table S3 Performance of different methodologies for the {p-BIB·DTMABr} (**1**) crystal structure.

{p-BIB·DTMABr} Method	a Å	b Å	c Å	Δa %	Δb %	Δc %
Experimental	7.884	14.580	11.560	--	--	--
revPBE-D3BJ	8.056	14.517	11.742	2.17	-0.43	1.57
SCAN	7.890	14.404	11.571	0.08	-1.21	0.10
SCAN-D3	7.754	14.035	11.294	-1.66	-3.73	-2.30
SCAN-D3BJ	7.732	13.975	11.256	-1.93	-4.14	-2.63

Table S4 Performance of different methodologies for the {p-BIB·TPABr} (**2**) crystal structure.

{p-BIB·TPABr} Method	a Å	b Å	c Å	Δa %	Δb %	Δc %
Experimental	9.933	8.802	14.570	--	--	--
revPBE-D3BJ	10.042	8.645	14.691	1.09	-1.78	0.83
SCAN	9.914	8.632	14.578	-0.20	-1.92	0.05
SCAN-D3	9.842	8.424	14.231	-0.92	-4.29	-2.33
SCAN-D3BJ	9.824	8.373	14.234	-1.10	-4.87	-2.30

Table S5 Interactions energies and distance of the I···Br$^-$ contact of optimized [*p*-BIB·Br]$^-$ and similar dimers extracted from optimized trimer (B3LYP-D3 and 6-311G+(d,p)/DGDZVP).

Complex	ΔE kJ mol^{-1}	d(I···Br$^-$) Å
[*p*-BIB:Br]$^-$	–103.3	3.030
[*p*-BIB:Br]$^-$-180	–100.3	3.168
[*p*-BIB:Br]$^-$ 139	–100.5	3.159
[*p*-BIB:Br]$^-$ 75	–98.6	3.229

Table S6 Uncorrected and corrected interaction energies (ΔE and ΔE_{BSSE}, respectively) of the dimers (single point calculations) using B3LYP-D3BJ/6-311G+(d,p)/DGDZVP or B3LYP-D3BJ/6-311G++(d,p)/DGDZVP.

Complex	6-311G+(d,p)/DGDZVP		6-311G++(d,p)/DGDZVP	
	ΔE kJ/mol	ΔE_{BSSE} kJ/mol	ΔE kJ/mol	ΔE_{BSSE} kJ/mol
trans type I I···I in 1	–5.6	–4.9	–5.6	–4.9
1−a	–21.9	–18.8	–21.9	–18.8
2−a	–12.0	–11.3	–12.0	–11.3
2−b	–13.8	–11.5	–13.8	–11.5
3−a	–13.9	–11.6	–13.9	–11.6
3−b	–7.2	–4.3	–7.2	–4.3

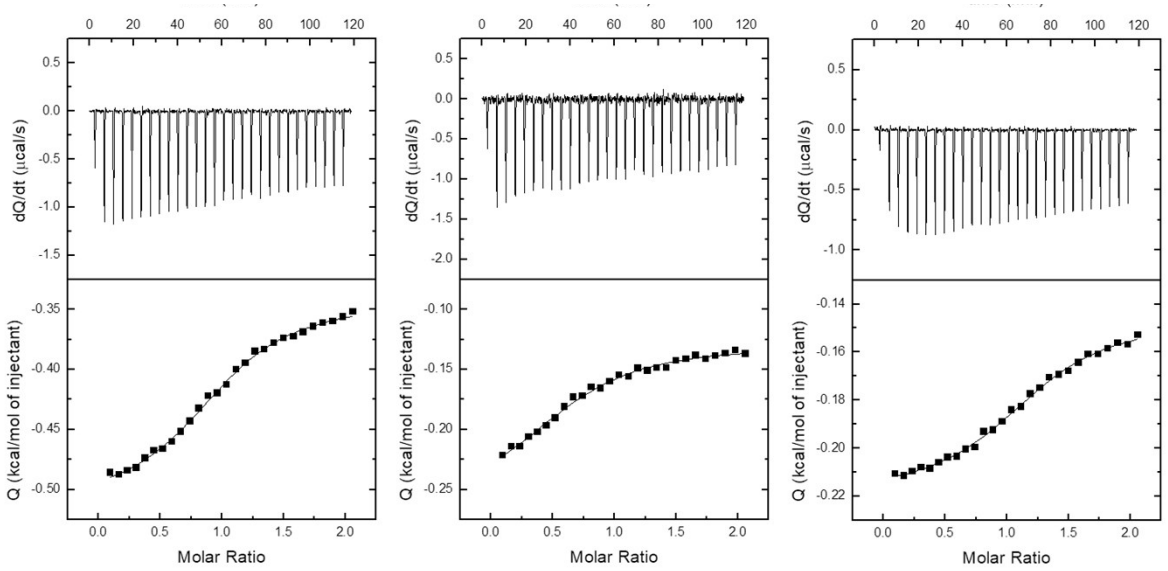

Figure S1 Calorimetric titrations of *p*-BIB with bromide salts: (left) TBABr, (center) TPABr, and (right) DTMABr. The upper panels show the thermograms (thermal power as a function of time) and the lower panels report the interaction isotherm (heat evolved associated with each injection, normalized per mole of titrant injected, as a fucntion of the molar ratio). Continuous lines represent the fitting to a 1:1 binding model.

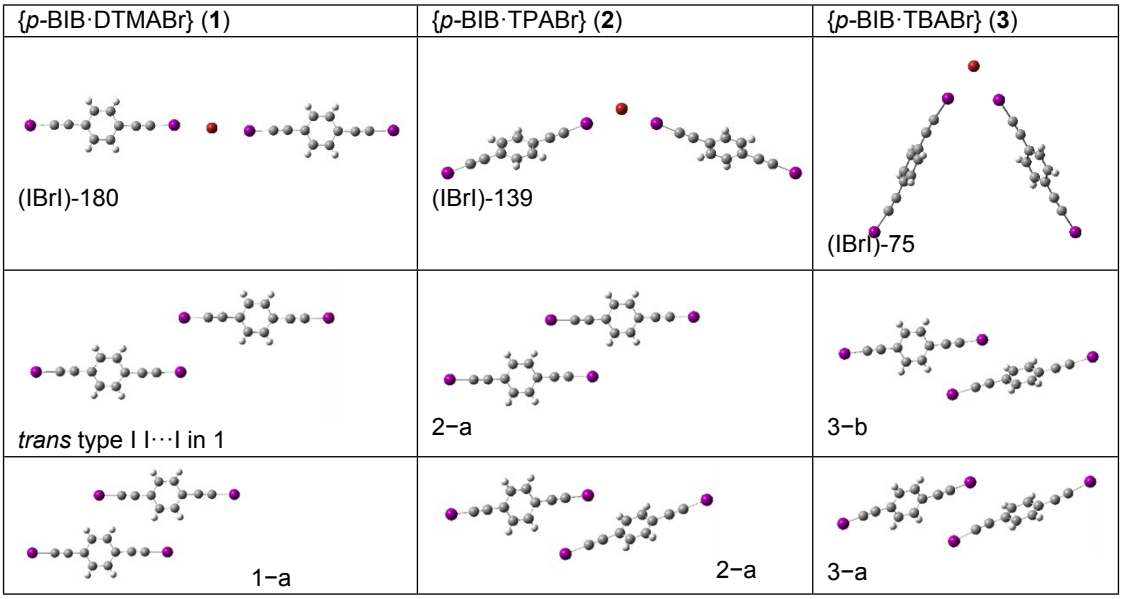

Figure S2 Dimers and trimers extracted of the crystal structures **1**, **2** and **3**.

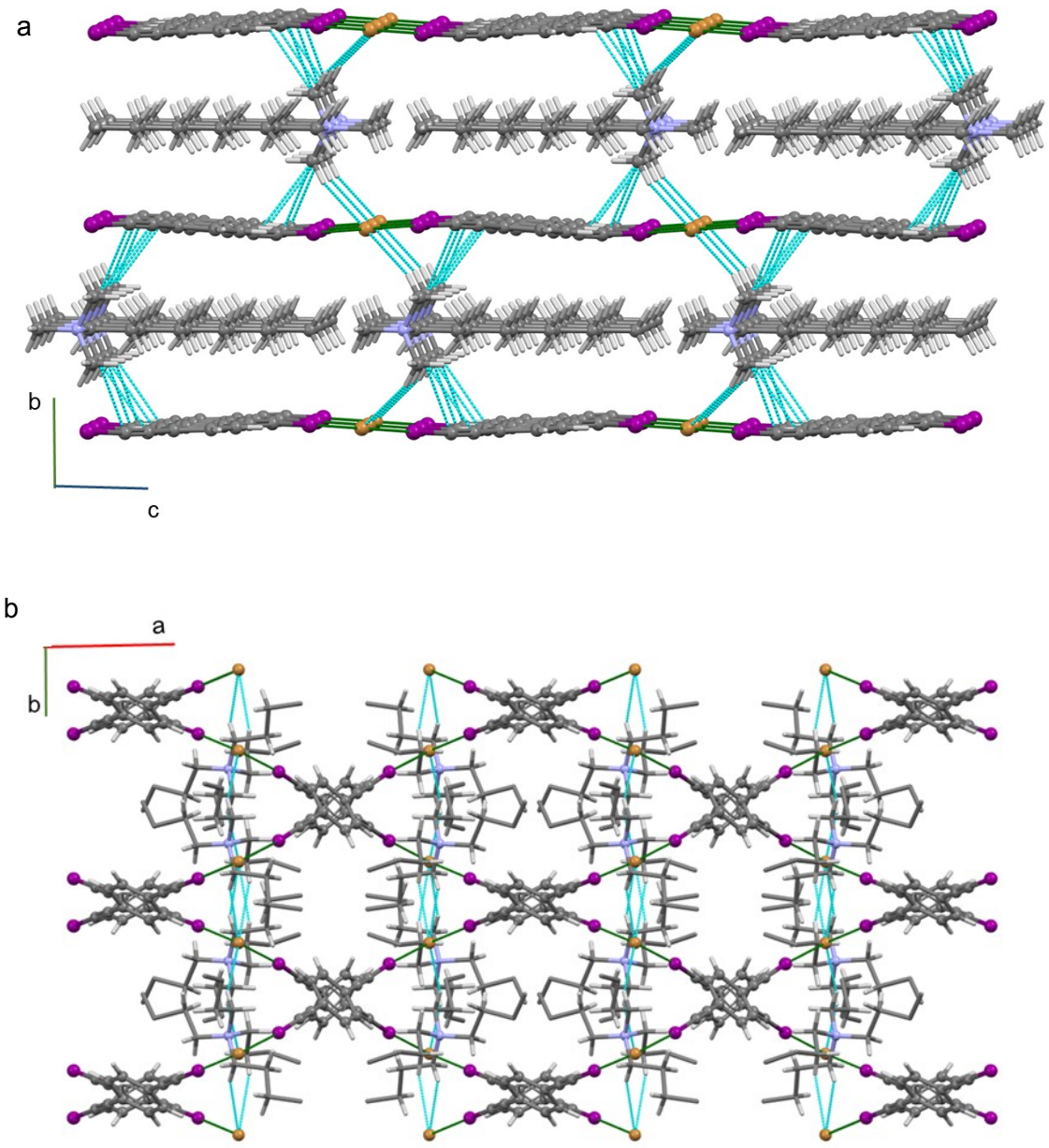

Figure S3 (a) Projection view of **1** along *a* axis showing the layered nature of anionic and cationic networks and (b) projection view of **3** along *c* axis. The dashed green line denotes the halogen bond and the dashed blue line denotes the hydrogen bond.

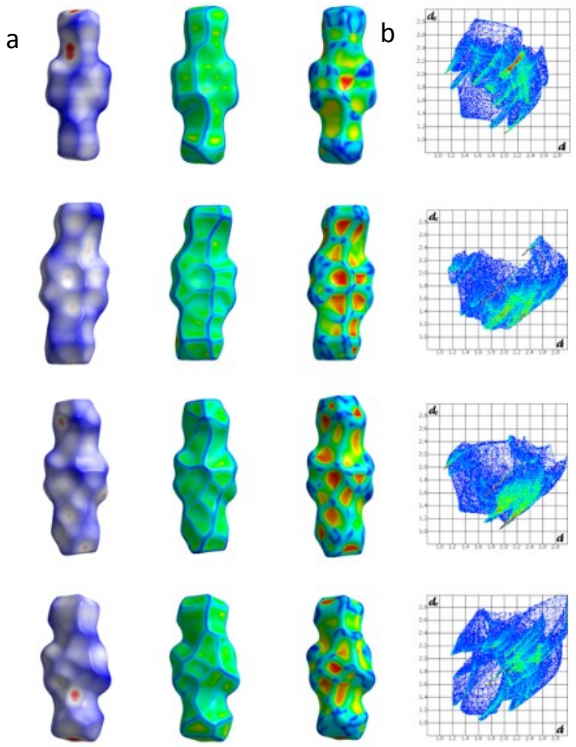

Figure S4 Hirshfeld surfaces (a) and 2D fingerprint plots (b) for the *p*-BIB molecules in *p*-BIB and **1** to **3** crystal structures. For each structure the Hirshfeld surface is shown mapped with d_{norm} (left), curvedness (center) and shape index (right).

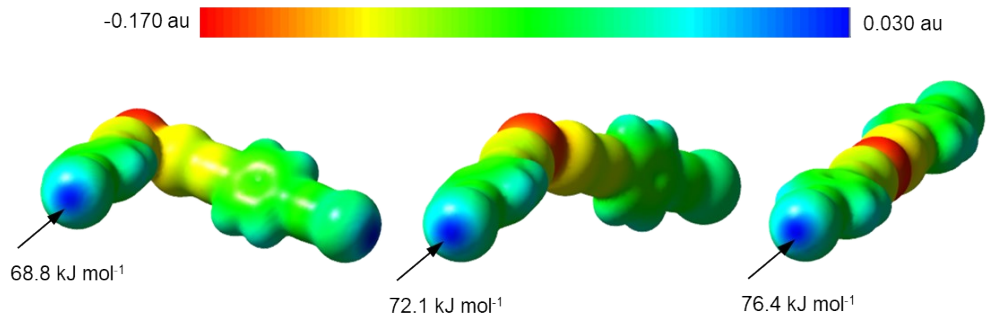

Figure S5 Computed electrostatic potential of the optimized geometry of (IBrI)-75 (left), (IBrI)-139 (middle) and (IBrI)-180 (right). Potentials are mapped on the respective electron density isosurfaces (0.002 e/Bohr^3).

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

(IBrI)-180; Energy (E_{au}), -31020.01562 Hartrees

I	3.16806600	0.00565200	-0.01561900
C	5.23277400	0.00930100	-0.02581800
C	6.45081600	0.01219200	-0.03066600
C	7.87102900	0.01595300	-0.03602400
C	8.60287600	0.07030000	1.17096200
H	8.06151300	0.10916700	2.10522100
C	9.99051100	0.07450200	1.16649800
H	10.53611800	0.11679500	2.09893400
I	15.35675200	0.03391200	-0.06198200
C	13.34417700	0.03003700	-0.05577200
C	12.13146300	0.02860800	-0.05210700
C	10.70739000	0.02436600	-0.04667300
C	9.98168200	-0.03012100	-1.25441900
H	10.52059900	-0.06903100	-2.19087600
C	8.59406700	-0.03421900	-1.24847500
H	8.04599500	-0.07632200	-2.17868100
Br	0.00000000	0.00000000	0.00000000
I	-15.35675200	-0.03391200	0.06198200
C	-13.34417700	-0.03003700	0.05577200
C	-12.13146300	-0.02860800	0.05210700
C	-10.70739000	-0.02436600	0.04667300
C	-9.98168200	0.03012100	1.25441900
H	-10.52059900	0.06903100	2.19087600
C	-8.59406700	0.03421900	1.24847500
H	-8.04599500	0.07632200	2.17868100
I	-3.16806600	-0.00565200	0.01561900
C	-5.23277400	-0.00930100	0.02581800
C	-6.45081600	-0.01219200	0.03066600
C	-7.87102900	-0.01595300	0.03602400
C	-8.60287600	-0.07030000	-1.17096200
H	-8.06151300	-0.10916700	-2.10522100
C	-9.99051100	-0.07450200	-1.16649800
H	-10.53611800	-0.11679500	-2.09893400

(IBrI)-139; Energy (E_{au}), -31020.01683 Hartrees

I	-2.95835700	1.59581200	0.00617600
C	-4.92002000	0.93725800	0.00870300
C	-6.07757600	0.55755100	0.00908600
C	-7.42951800	0.12246100	0.00668200
C	-7.91028800	-0.76942900	0.99086400
H	-7.22773500	-1.12095800	1.75105000
C	-8.33502300	0.57190900	-0.98010100
H	-7.97955000	1.25389800	-1.73896200
I	-14.57131400	-2.11962900	0.00501600
C	-12.64837300	-1.52726100	0.00391200
C	-11.49083800	-1.16553100	0.00391100
C	-10.13264100	-0.73734900	0.00368200
C	-9.65744100	0.15177900	-0.98218300
H	-10.33817500	0.50546700	-1.74397900
C	-9.23260900	-1.19045800	0.99003200
H	-9.58530900	-1.87271400	1.75093300
Br	0.00000600	2.70247600	0.00007000
I	2.95834900	1.59575800	-0.00618900
C	4.91997500	0.93709600	-0.00880300
C	6.07751500	0.55734000	-0.00921800
C	7.42947800	0.12231300	-0.00677100
C	7.91035700	-0.76943300	-0.99103100
H	7.22787400	-1.12089700	-1.75131000
C	8.33489400	0.57168300	0.98012800
H	7.97933700	1.25356400	1.73904700
I	14.57134100	-2.11956500	-0.00499400
C	12.64839500	-1.52721100	-0.00388000
C	11.49085700	-1.16549100	-0.00387500

C	10.13264000	-0.73737400	-0.00368900
C	9.65733000	0.15161200	0.98225200
H	10.33799500	0.50524000	1.74413800
C	9.23269800	-1.19040100	-0.99015800
H	9.58548300	-1.87254600	-1.75112000

(IBrI)-75; Energy (E_{au}), -31020.01652 Hartrees

Br	-0.01764000	-6.80835200	0.00581300
I	-1.98701400	-4.25045900	0.00138500
C	-3.20027100	-2.58115500	-0.00241600
C	-3.91098100	-1.59207900	-0.00535600
C	-4.73457600	-0.43517400	-0.00970000
C	-4.26601100	0.78840100	-0.53772700
H	-3.26429900	0.83064700	-0.94022800
C	-6.04578700	-0.47303700	0.51423500
H	-6.41564400	-1.40296800	0.92149700
I	-9.06448500	5.67032700	-0.03039000
C	-7.90433400	4.02653300	-0.02534400
C	-7.20282100	3.03727800	-0.02178300
C	-6.37797100	1.87637800	-0.01782500
C	-6.85047700	0.65748700	0.51058000
H	-7.85199200	0.61238100	0.91534900
C	-5.06967300	1.91962300	-0.54211100
H	-4.69620300	2.84877200	-0.94951100
I	9.10332500	5.61759800	0.02788500
C	7.93289900	3.98109000	0.02375900
C	7.22411700	2.99702400	0.02028200
C	6.39034100	1.84254900	0.01600500
C	6.54955200	0.84137700	-0.96406300
H	7.31652400	0.95897800	-1.71695200
C	5.73548900	-0.28237700	-0.96854700
H	5.86409500	-1.04455300	-1.72350000
I	1.95683800	-4.25373900	0.00070200
C	3.17741800	-2.58980400	-0.00023800
C	3.89439200	-1.60519900	0.00117600
C	4.72708800	-0.45492900	0.00548500
C	4.57161100	0.55115300	0.98485800
H	3.80288500	0.43175300	1.73458000
C	5.38501400	1.67532700	0.99058100
H	5.25266200	2.43697600	1.74635200

[*p*-BIBBr]$^{-}$; Energy (E_{au}), -16796.90333 Hartrees

Br	7.60580600	-0.00002300	0.00000500
I	4.57614900	-0.00002200	-0.00004500
C	2.46327400	0.00000100	-0.00012800
C	1.24158800	0.00001700	-0.00017900
C	-0.17676500	0.00005100	-0.00012200
C	-0.90796800	1.21056000	-0.00008300
H	-0.36282800	2.14346900	-0.00010100
C	-0.90802700	-1.21042100	-0.00008900
H	-0.36293400	-2.14335800	-0.00011000
I	-7.66759400	-0.00005800	0.00010700
C	-5.65476400	0.00008500	0.00008800
C	-4.44158200	0.00016000	0.00005000
C	-3.01796400	0.00012200	-0.00000900
C	-2.29526800	-1.21128800	-0.00003400
H	-2.83743400	-2.14697400	-0.00001200
C	-2.29520900	1.21149600	-0.00002900
H	-2.83732800	2.14720900	-0.00000300