Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information for: Formation of the non-classical interhalide anion $[I_2Cl]^-$ in methyl-bambus[6]uril cavity

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1 General information

Methyl-bambus[6]urils (chloride and empty forms) were prepared and purified as described elswhere[1,2]. The resutling solids does not present a porous structure and forms hexagonal crystals in tabular habit, as observed by electron microscopy (see fig S1). All the other reactants and solvents were used without any previously treatment. Weight measurements were performed on a AT21 Comparator (Mettler Toledo) semi-analytical balance (readability of 1 μg). FTIR spectra were obtained on a Shimadzu IR Prestige 21 using KBr powder. Thermal analyses (TGA-DTA) were performed on a TA Instruments SDT Q600 equipment under synhtetic air (10°C min^{-1}), from 30 to 600°C. FT-RAMAN spectra were obtained on a Bruker RAMII using a 1064 nm laser line (100 mW) from 50 to 400 cm^{-1}. UV-vis spectra were collected on a Shimadzu UV1280 spectrophotometer using 1 cm path quartz cuvettes. ^{1}H NMR spectra were obtained on Bruker Ultra Shield DRX-400 and DRX-500 equipments. Conductometric experiments were performed on a Tecnopon MCA 150 conductimeter with cell constant equal to 1.2. Scanning electron microscopy were realized on a Carl Zeiss EVO 50 using secondary electrons contrast mode (see S1).

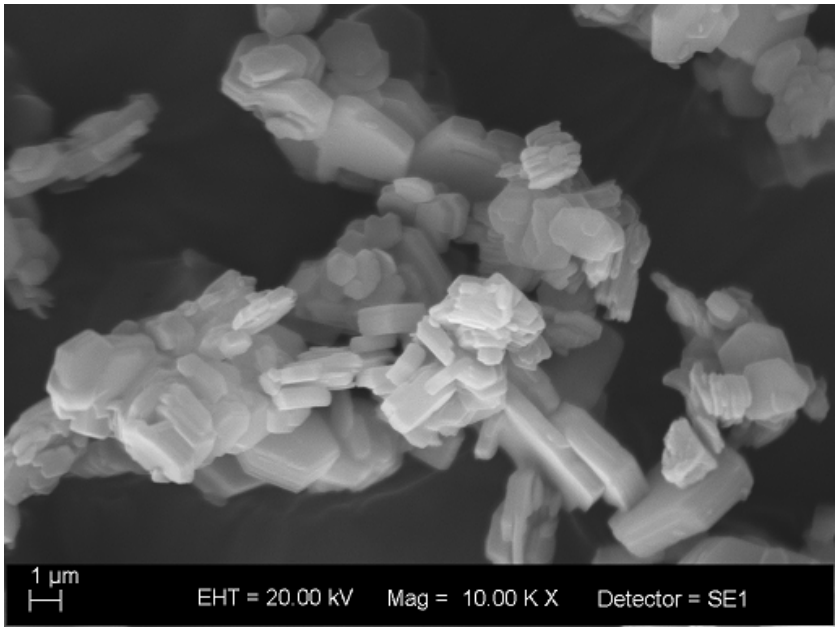

Figure S1: Scanning electron microscopy of solid **MeBU[6]** showing hexagonal crystals in tabular habit.

2 Characterization of $H^+(Cl^-@MeBU[6])$ and MeBU[6]

^{1}H NMR and FTIR spectra of Cl^-@**MeBU[6]** and **MeBU[6]** were compared with the ones reported in the literature[1] (see S2-S5). Note that the correct formula for Cl^-@**MeBU[6]** is $H^+(Cl^-$@**MeBU[6]**) according to IUPAC, but we use Cl^-@**MeBU[6]** for simplicity. Data for Cl^-@**MeBU[6]**: FTIR (KBr): 1722 (ν C=O urea), 1703 (ν C=O 1,3-dimethylurea), 1402 (δ C-H of -CH_3), 1260 (δ C-H of -CH_2-), 1129 (ν C-C), 793 (ν N-C-N) cm^{-1}H^1; ^{1}H NMR ($CDCl_3/CD_3OD$ 1:1 mol mixture, 500 MHz, 23°C): δ= 5.36 (s, 12H), 5.14 (s, 12H), 3.09 (s, 36H) ppm. Data for **MeBU[6]**: FTIP (KBr): 1721 (ν C=O urea), 1701 (ν C=O 1,3-dimethylurea), 1400 (δ C-H of -CH_3), 1265 (δ C-H of -CH_2-), 1133 (ν C-C), 795 (ν N-C-N) cm^{-1}; ^{1}H NMR (DMF d_7, 500 MHz, 23°C): δ= 5.19 (s, 12H), 5.15(s, 12H), 3.11 (s, 36H) ppm.

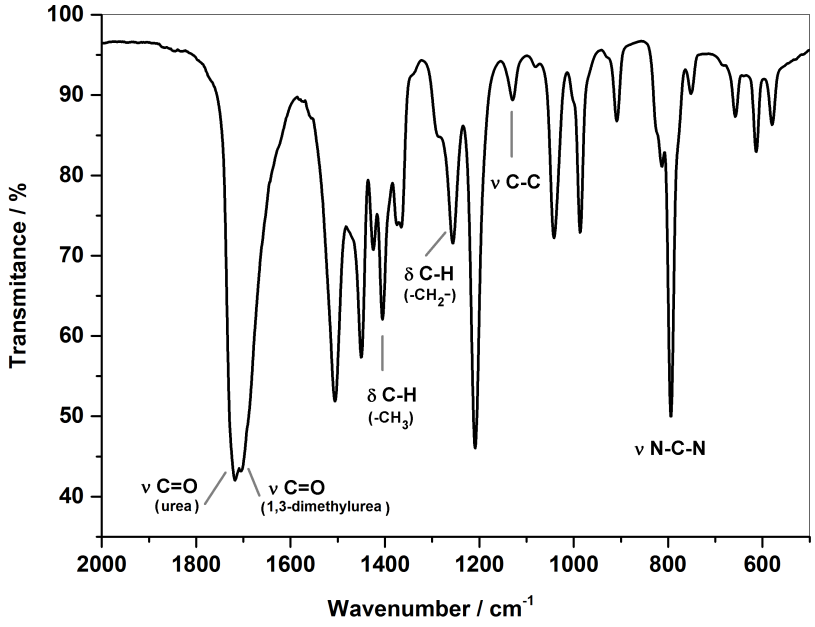

Figure S2: FTIR spectrum of Cl^{-}@**MeBU[6]** in KBr pellet.

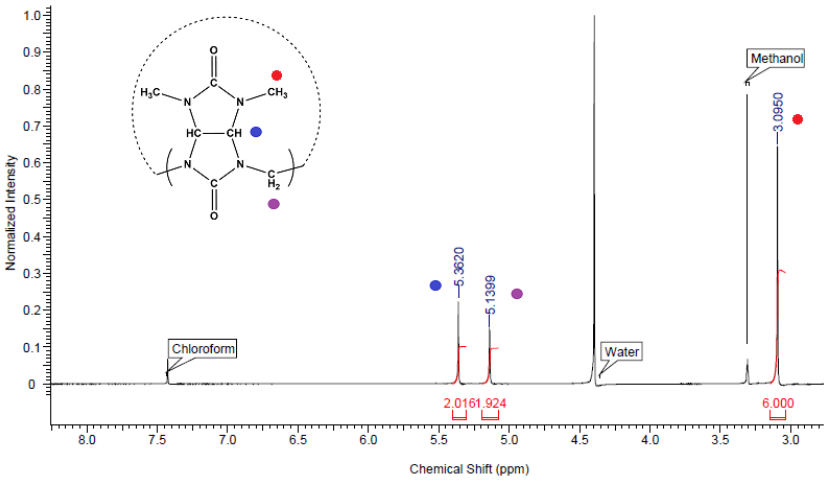

Figure S3: H^1 NMR spectrum of Cl^{-}@**MeBU[6]** in $CDCl_3/CD_3OD$ 1:1 mol mixture, 500 MHz, 23°C.

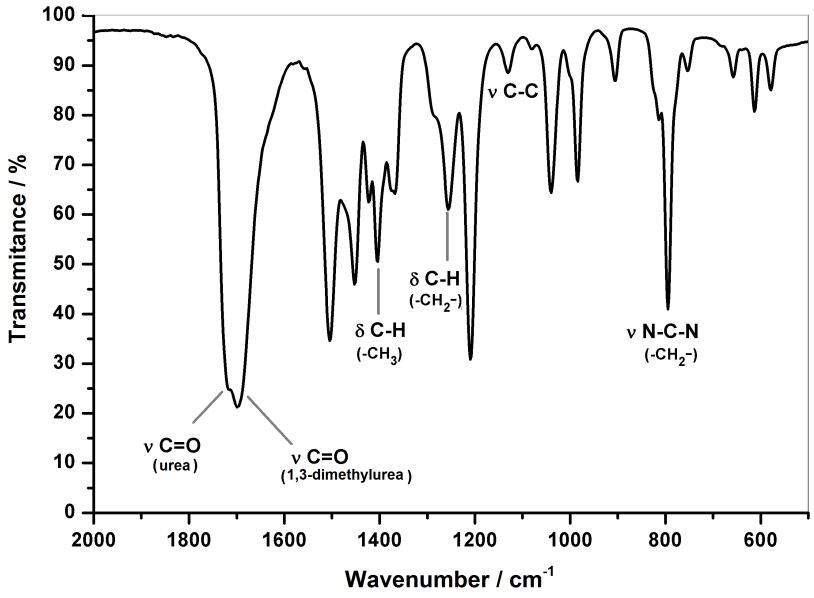

Figure S4: FTIR spectrum of **MeBU[6]** in KBr pellet.

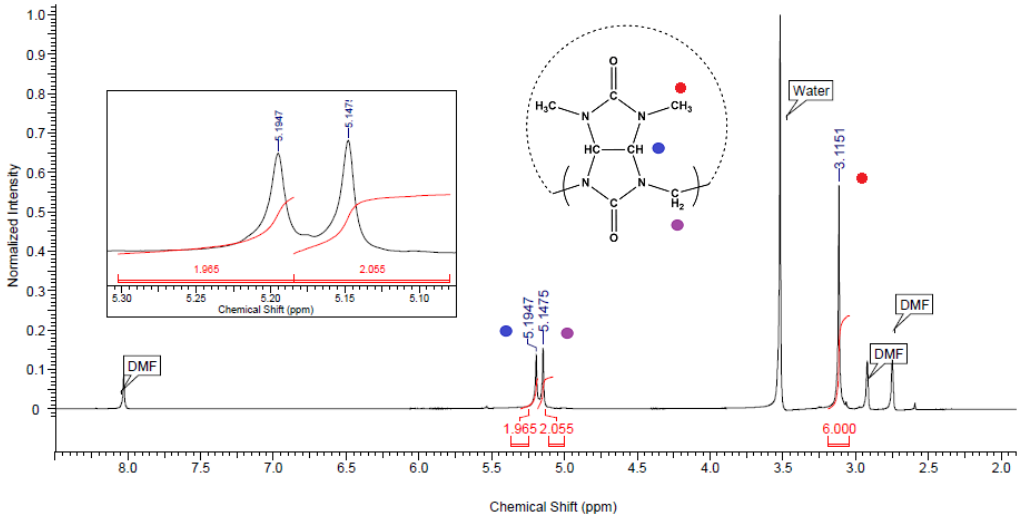

Figure S5: H^1 NMR spectrum of **MeBU[6]** in DMF d_7, 500 MHz, 23°C.

Cl^-@**MeBU[6]** TGA-DTA analysis was carried out to calculate the number of hydration molecules in the solid. From 30 to 132 °C, the compound

looses 21.1 μmol of adsorbed water and at 270 °C the residual mole number of water-free Cl^-@**MeBU[6]** is 3.8 μmol. Accordingly, its aproximate formula is $H^+(Cl^-$@**MeBU[6]**$).(H_2O)_{5.5}$.

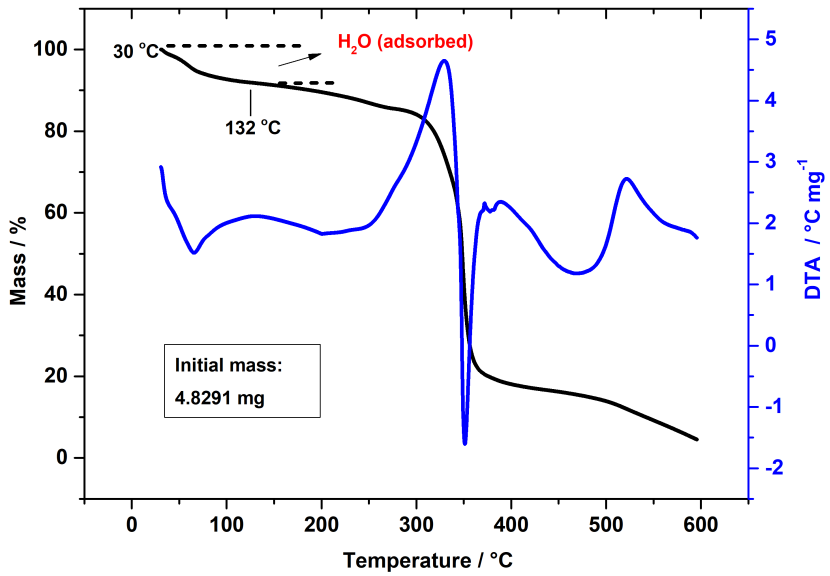

Figure S6: TGA-DTA analysis of Cl^-@**MeBU[6]** under synthetic air flow using a temperature rate of 10°C min^{-1}.

3 Synthesis of H^+(I_2Cl^-@MeBU[6])

The hetero-atomic trihalide caviplex was prepared by placing a small flask containing 35.5 μmol of solid Cl^-@**MeBU[6]** (40.0 mg) into a larger flask containing 1 g of I_2. The sample was kept in contact with iodine gas for one week at 27°C and then left in open air for one hour prior to measurements to remove the excess of iodine (see S7 and figure 3 in the article). FTIR (KBr): 1722 (ν C=O urea), 1703 (ν C=O 1,3-dimethylurea), 1404 (δ C-H of -CH_3), 1256 (δ C-H of -CH_2-), 1133 (ν C-C), 792 (ν N-C-N) cm^{-1}; Raman : I_2Cl^-@**MeBU[6]**: 65 (I_2Cl^-—I_2, ν I-I of I_2Cl^-), 108 (I_2—I_2Cl^-, ν I-I of I_2Cl^-), 146 (I_2Cl^-—I_2, ν I-I of I_2), 180 (I_2Cl^-—I_2, ν I-Cl) and 266 (I_2—I_2Cl^-, ν I-Cl) cm^{-1}.

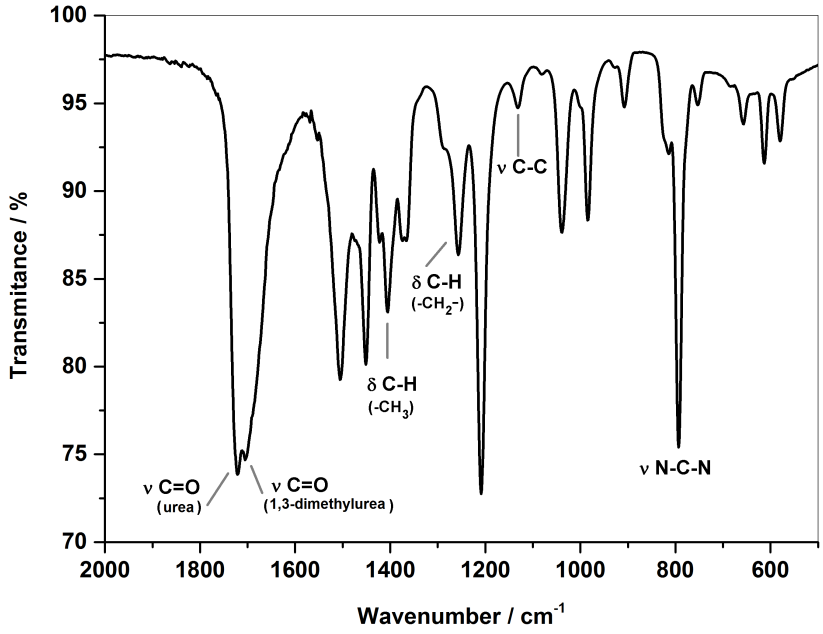

Figure S7: FTIR spectrum of $[I_2Cl]^-$@**MeBU[6]** in KBr pellet.

4 Adsorption/desorption kinetics

Iodine gas adsorption experiments were realized placing a small flask containing 35.5 μmol of solid **MeBU[6]** (39.0 mg) or Cl^-@**MeBU[6]** (40.0 mg) into a larger flask containing 1 g of I_2. The macrocycle samples were kept in contact with iodine gas from one to five days at 27°C and each sample was left in open air for one hour prior to weight measurements. The molar adsorption capacity (Q) (with and without chloride ion) was calculated using the equation 1.

$$Q = \frac{n_{\mathrm{I}}}{n_{\mathrm{BU}}} \tag{1}$$

where n_{I} and n_{BU} are respectively iodine and **MeBU[6]** or Cl^-@**MeBU[6]** mole amount. To analyze the adsorption process we adopted a pseudo-first order approach[3,4] (halogens in large excess), which is given by equation 2

$$Q_t = Q_e(1 - e^{-k_1 t}) \tag{2}$$

By plotting a graph of molar adsorption capacity *versus* time we calculated the molar adsorption capacity at the equilibrium (Q_e) and the pseudo-

first order constant k_1 values (see S8 and S9).

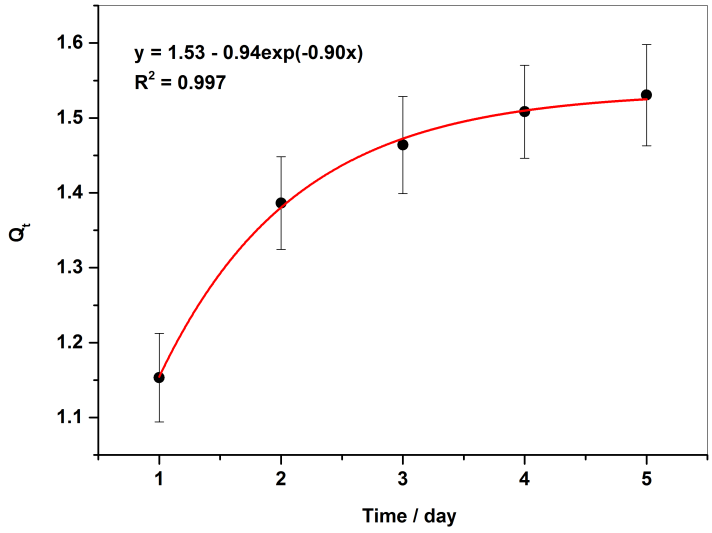

Figure S8: Adsorption curve of iodine in Cl^-@**MeBU[6]**, at 27°C.

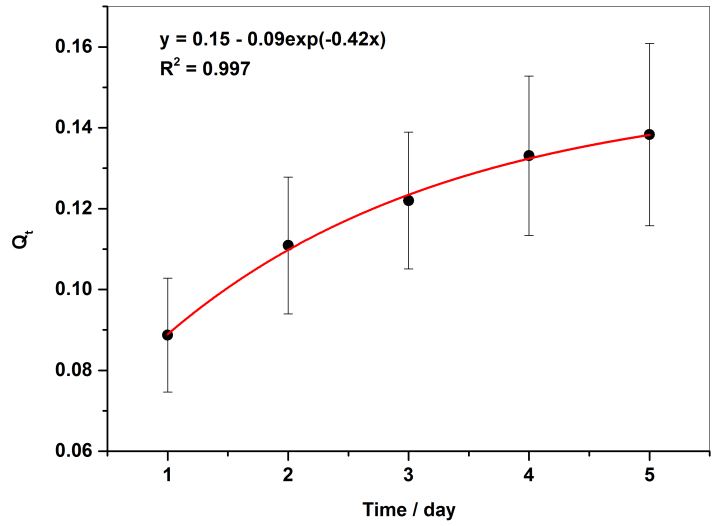

Figure S9: Adsorption curve of iodine in **MeBU[6]**, at 27°C.

For iodine gas desorption experiments, we placed a small flask containing 35.5 μmol of solid **MeBU[6]** (39.0 mg) or Cl^-@**MeBU[6]** (40.0 mg) into a

larger flask containing 1 g of I_2. After one day of exposure, the macrocycle samples were left in open air from one to five days at 27°C and weight measurements were realized at intervals of one day. The desorption processes were evaluated by a first-order exponential decay[3] using the equation 3

$$Q_t = Q_0 e^{-k_d t} \tag{3}$$

By plotting a graph of molar adsorption capacity *versus* time we calculated the molar adsorption capacity at the equilibrium after desorption ($Q_{e,d}$) and the decay constant k_d values (see S10 and S11). The desorption half-life time was calculated using the equation 4

$$t_{1/2} = \frac{\ln 2}{k_d} \tag{4}$$

All the experiments of iodine gas adsorption and desorption were carried out in triplicate.

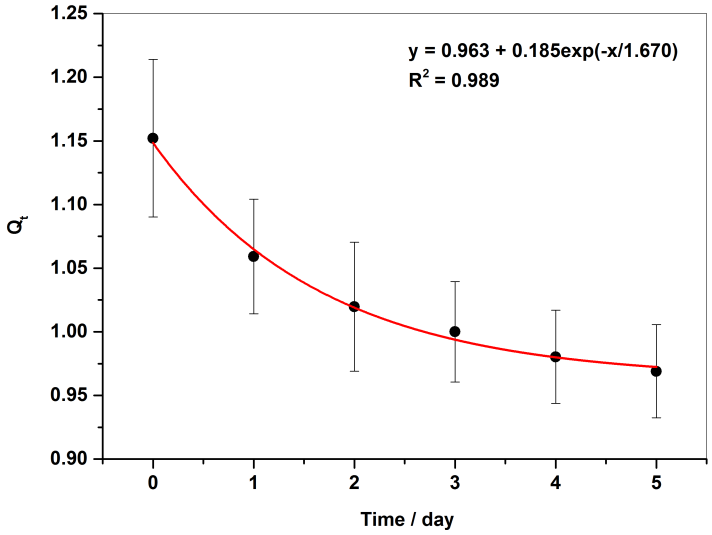

Figure S10: Desorption curve of iodine in Cl^-@**MeBU[6]**, at 27°C.

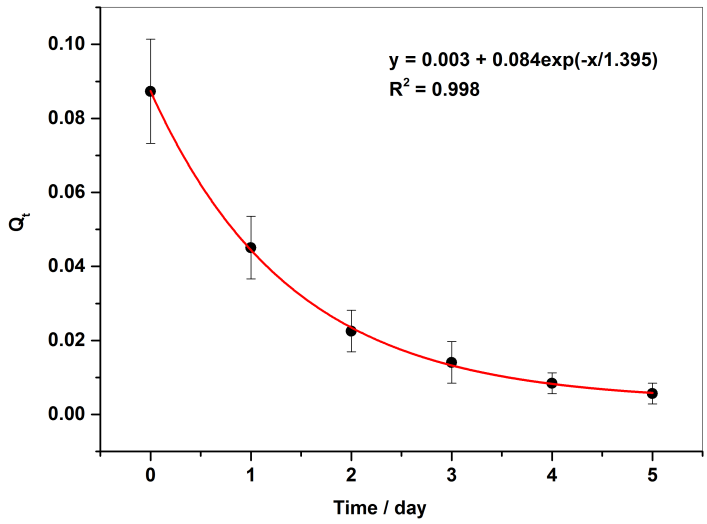

Figure S11: Desorption curve of iodine in **MeBU[6]**, at 27°C.

5 Titrations

UV-vis titrations were performed by adding fixed amounts (10 μL) of a Cl^-@**MeBU[6]** solution (28 mmol L^{-1}, in $CHCl_3/CH_3OH$ mixture 1:1 mol) to 3 mL of iodine (0.55 mmol L^{-1}, in $CHCl_3/CH_3OH$ mixture 1:1 mol), at 27°C. The same procedure was realized with **MeBU[6]** suspension (0.3 mg/10 μL). Also, we have titrated 3 mL of iodine (0.55 mmol L^{-1}, in $CHCl_3/CH_3OH$ mixture 1:1 mol), at 27°C, with tetramethylammonium chloride to confirm the formation of I_2Cl^- (see S12

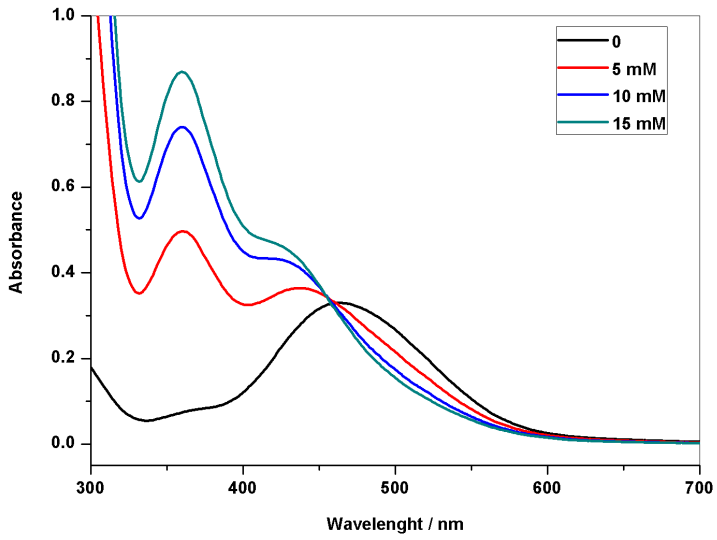

Figure S12: UV-Vis spectra of iodine solution (0.5 mmol L−1 in $CH_3OH/CHCl_3$ 1:1 mol) after successive additions of tetramethylammonium chloride showing a new band at 360 nm related to $[I_2Cl]^-$ formation (at 27 ^oC).

To calculate the binding constant, we performed a titration using fixed amounts (20 μL) of iodine in large excess (250 mmol L^{-1}, in a $CDCl_3/CD_3OD$ 1:1 mol mixture) and 1 mL of Cl^-@MeBU[6] 5 mmol L^{-1} (in $CDCl_3/CD_3OD$ 1:1 mol mixture), at 23°C. The binding constant (K_{11}) was determined according to the method described in literature[5]. Considering a 1:1 host-guest pair (H-G), the chemical shift varies with guest concentration ([G], in mol.L^{-1}) during the titration, according to the following equation (5):

$$\frac{1}{\Delta\delta} = \frac{1}{\Delta\delta_{11} K_{11}[G]} + \frac{1}{\Delta\delta_{11}} \tag{5}$$

where $\Delta\delta$ is the difference between the initial and last chemical shifts, $\Delta\delta_{11}$ is the difference between the chemical shifts of (H-G) and (H) and K_{11} is the 1:1 association constant. Our calculations were realized using the chemical shift changes of the methylene brigde hydrogens (5.14 ppm). By plotting a graph of $1/\Delta\delta$ *versus* 1/[G] we calculated the K_{11} value (see S14 and S15).

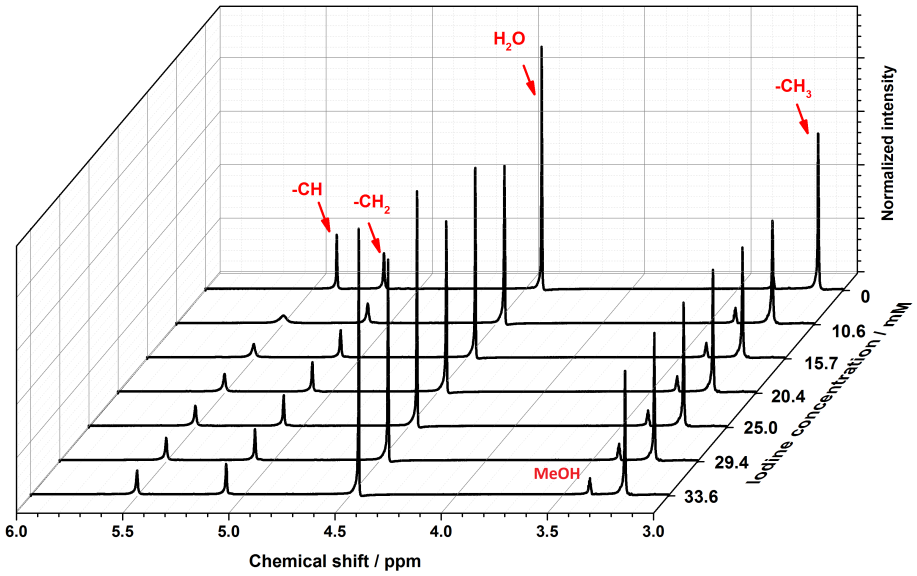

Figure S13: H^1 NMR titration of Cl^-@**MeBU[6]** 5 mmol L^{-1} with iodine 250 mmol L^{-1}, in $CDCl_3/CD_3OD$ 1:1 mol mixture, 500 MHz, 23°C. CH_3OH (MeOH) was produced due to proton exchange of CD_3OD with water.

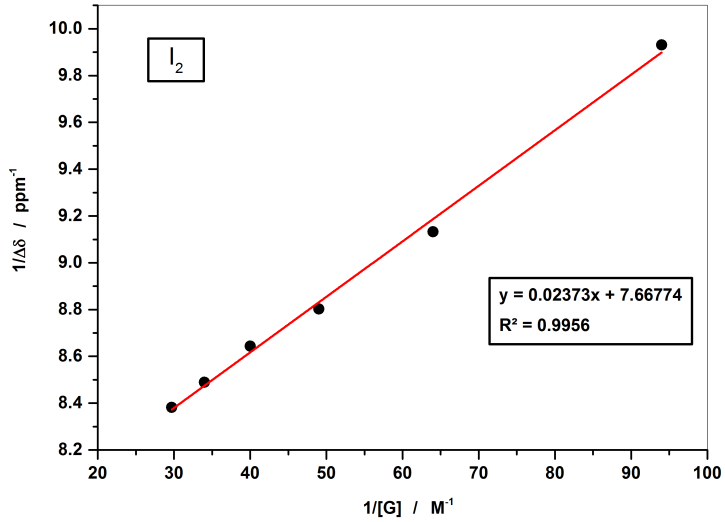

Figure S14: The linear trend of $1/\Delta\delta$ with respect to $1/[G]$ for Cl^-@**MeBU[6]** titration with iodine.

6 Computational calculations

All computational calculations were performed using the ORCA program package (version 4.1.1)[6]. The BP86 density functional[7,8] in conjunction with the resolution-of-the-identity (RI) approximation[9] was applied through this work. To take into account dispersion effects, Grimme's dispersion (D3) correction[10,11] with the Becke-Johnson (BJ) damping parameter[12] was considered. The Ahlrichs def2-SVP basis set[13,14] along with the def2-SVP/J Coulomb fitting basis was applied for the resolution of identity[15,16]. In the explored potential energy surfaces, all the structures were characterized as minima presenting only non-imaginary frequencies.

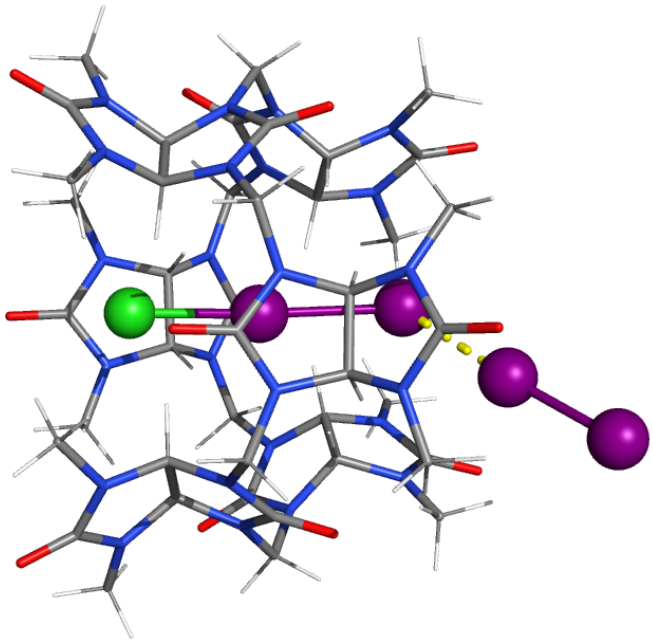

Figure S15: Optimized geometry for $I_2 \cdots [I_2Cl]^-$ and **MeBU[6]**.

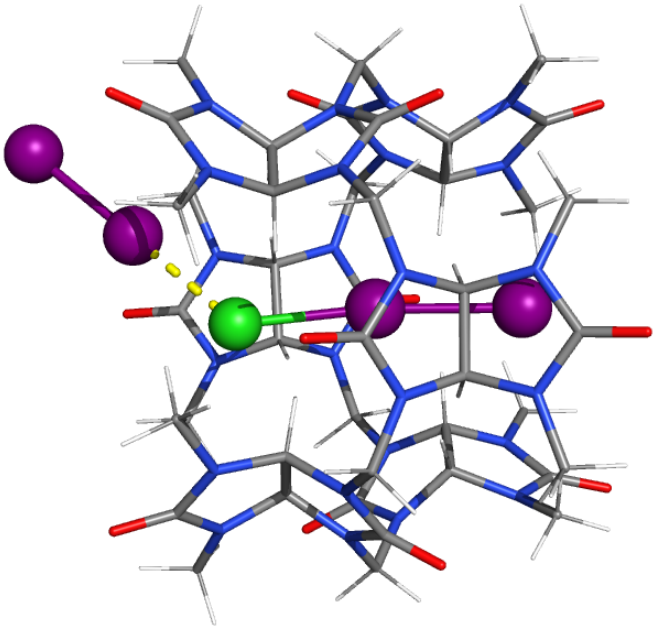

Figure S16: Optimized geometry for $[I_2Cl]^- \cdots I_2$ and **MeBU[6]**.

6.1 Cartesian coordinates for $I_2 \cdots [I_2Cl]^-$ with MeBU[6]

N	4.194844	1.195282	0.463878
C	4.366762	2.516482	−0.098845
H	4.823455	3.198350	0.643129
H	5.050386	2.396468	−0.961506
C	3.535035	0.926307	1.743500
H	2.520975	1.383364	1.751534
N	4.275877	1.280175	2.927033
C	4.568318	2.629855	3.359348
H	4.588180	2.654255	4.466550
H	3.796787	3.323696	2.973959
H	5.560892	2.984961	2.997851
C	4.753111	0.166935	3.617024
O	5.402002	0.187305	4.656734
N	4.317161	−0.964193	2.935835
C	4.427350	−2.293086	3.500349
H	4.563824	−2.198556	4.595598
H	3.512666	−2.874545	3.267683
H	5.303804	−2.850431	3.097432
C	3.491095	−0.640727	1.794639
H	2.464871	−1.043164	1.922701
N	4.028884	−1.033938	0.497279
C	4.397702	0.042081	−0.287282
O	4.821859	−0.006558	−1.444328
N	2.753376	−2.890528	−0.432162
C	4.032659	−2.397872	0.014276
H	4.373838	−3.069655	0.824772

H	4.753790	−2.448267	−0.824359
C	2.219283	−2.703488	−1.784780
H	2.015112	−1.628776	−1.974031
N	3.023043	−3.259820	−2.841253
C	3.886310	−2.425931	−3.663770
H	4.570791	−1.829518	−3.031552
H	3.294183	−1.725427	−4.298656
H	4.463209	−3.093919	−4.330247
C	2.419480	−4.399323	−3.397808
O	2.840647	−5.043694	−4.347503
N	1.246021	−4.644976	−2.688375
C	0.280254	−5.628418	−3.129815
H	0.241507	−6.513688	−2.456627
H	−0.731179	−5.173658	−3.171060
H	0.579172	−5.968144	−4.139938
C	0.926383	−3.587080	−1.757180
H	0.002798	−3.049791	−2.069396
N	0.816586	−3.995769	−0.365736
C	1.905617	−3.606608	0.395108
O	2.084191	−3.848921	1.591767
N	−1.448885	−3.791245	0.498959
C	−0.339918	−4.661507	0.188289
H	−0.014682	−5.174335	1.113546
H	−0.713357	−5.413530	−0.531706
C	−1.508427	−2.945285	1.691639
H	−0.653173	−2.241458	1.718418
N	−1.610900	−3.653763	2.942772
C	−0.450429	−3.861992	3.797071
H	−0.742620	−4.553691	4.608672
H	−0.096145	−2.907180	4.248536
H	0.385201	−4.287573	3.211217
C	−2.883530	−3.514179	3.507032
O	−3.249419	−3.956434	4.588781
N	−3.653084	−2.748679	2.632774
C	−5.022349	−2.385582	2.932304
H	−5.166873	−2.457983	4.027965
H	−5.226050	−1.355606	2.580093
H	−5.754292	−3.068465	2.444829
C	−2.886216	−2.220230	1.525911
H	−2.808444	−1.109603	1.586125
N	−3.318791	−2.609650	0.193478
C	−2.448167	−3.510722	−0.413500
O	−2.551506	−3.963694	−1.554802
N	−4.296912	−0.662031	−0.872587
C	−4.461007	−2.050623	−0.493345
H	−5.364245	−2.095501	0.144619
H	−4.612215	−2.676251	−1.393686
C	−3.302371	−0.228361	−1.856164
H	−2.329894	−0.717450	−1.633180
N	−3.663723	−0.399135	−3.234743
C	−3.753041	−1.680038	−3.902629
H	−4.775020	−2.118801	−3.841177
H	−3.040512	−2.392025	−3.441124
H	−3.500435	−1.546137	−4.971390
C	−3.997398	0.800645	−3.854387
O	−4.416917	0.939921	−4.995686
N	−3.726779	1.824673	−2.943427
C	−4.124530	3.194293	−3.178753
H	−5.151033	3.403969	−2.798825
H	−3.423939	3.890089	−2.677402
H	−4.119724	3.369242	−4.271210
C	−3.272068	1.326786	−1.667457

H	−2.256379	1.716316	−1.423282
N	−4.163934	1.550784	−0.536708
C	−4.707720	0.370144	−0.042814
O	−5.417716	0.266937	0.959257
N	−2.898590	3.156745	0.747791
C	−4.194545	2.780754	0.234464
H	−4.917886	2.602906	1.054882
H	−4.539286	3.636508	−0.377988
C	−2.099946	2.315358	1.633440
H	−2.004640	1.294667	1.197960
N	−2.532607	2.249984	3.005795
C	−3.387809	1.178467	3.487232
H	−3.641569	1.393821	4.541235
H	−2.860649	0.195752	3.456236
H	−4.311060	1.106377	2.883794
C	−1.578614	2.798240	3.870201
O	−1.604223	2.745248	5.091547
N	−0.581610	3.401160	3.093880
C	0.726135	3.629533	3.679882
H	0.581274	3.787475	4.764699
H	1.386586	2.742982	3.538779
H	1.224737	4.508572	3.230686
C	−0.727286	3.070302	1.696982
H	0.124816	2.439513	1.356206
N	−0.911616	4.187539	0.780248
C	−2.167270	4.196798	0.188767
O	−2.558862	4.975452	−0.681429
N	1.212750	4.281517	−0.352638
C	0.165335	5.029892	0.307137
H	0.654725	5.569717	1.142325
H	−0.298610	5.765927	−0.380071
C	0.972249	3.387451	−1.482610
H	0.131844	2.698975	−1.233505
N	0.755167	4.011628	−2.761087
C	−0.574606	4.299784	−3.263620
H	−1.105013	5.026484	−2.618837
H	−1.191597	3.372400	−3.330716
H	−0.458647	4.713006	−4.282902
C	1.801769	3.741581	−3.654018
O	1.837542	4.051780	−4.837299
N	2.776924	3.033136	−2.959472
C	3.915388	2.438460	−3.628333
H	4.849473	3.019983	−3.461098
H	4.079251	1.409524	−3.248988
H	3.708923	2.422250	−4.716396
C	2.343955	2.646693	−1.639364
H	2.258964	1.539959	−1.562275
N	3.134850	3.145951	−0.528055
C	2.444567	4.061145	0.253105
O	2.845009	4.581229	1.294802
Cl	0.164709	−0.071777	2.471191
I	0.164584	−0.098931	−0.165241
I	0.076816	0.281151	−3.115305
I	−0.039488	−2.202063	−5.023316
I	−0.124455	−4.276922	−6.922575

6.2 Cartesian coordinates for $[I_2Cl]^- \cdots I_2$ with MeBU[6]

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N	4.012046	0.855680	0.618434

C	4.288684	2.198838	0.164511
H	4.651631	2.822342	1.003092
H	5.082757	2.113575	−0.602405
C	3.354736	0.534373	1.880053
H	2.368192	1.044093	1.935853
N	4.135296	0.785499	3.065917
C	4.386876	2.100731	3.616846
H	4.426309	2.019292	4.720626
H	3.574625	2.794785	3.323208
H	5.355422	2.525167	3.267192
C	4.422611	−0.377834	3.773697
O	5.002758	−0.451373	4.849217
N	3.893004	−1.446092	3.051002
C	3.928934	−2.802826	3.549335
H	3.964171	−2.768700	4.655746
H	3.031275	−3.353388	3.208397
H	4.823879	−3.364822	3.196243
C	3.239800	−1.031656	1.837860
H	2.188383	−1.388530	1.810453
N	3.921990	−1.378578	0.587684
C	4.342138	−0.265111	−0.125704
O	4.899539	−0.269836	−1.225213
N	2.748317	−3.216431	−0.491979
C	3.998373	−2.714388	0.037421
H	4.312783	−3.435990	0.815623
H	4.765394	−2.679905	−0.761428
C	2.077145	−2.662990	−1.664582
H	1.956088	−1.566538	−1.540094
N	2.676655	−2.957543	−2.942978
C	3.604775	−2.046406	−3.588615
H	4.534605	−1.928479	−3.003314
H	3.153356	−1.035371	−3.713493
H	3.830768	−2.465149	−4.586623
C	1.862255	−3.793658	−3.716399
O	2.073508	−4.144955	−4.870742
N	0.753134	−4.129636	−2.949027
C	−0.301083	−4.986272	−3.443949
H	−0.183897	−6.040115	−3.102745
H	−1.286008	−4.624546	−3.087137
H	−0.261414	−4.976861	−4.550806
C	0.713301	−3.439118	−1.683783
H	−0.175743	−2.769023	−1.624894
N	0.775448	−4.275390	−0.495509
C	1.958666	−4.110031	0.214321
O	2.250186	−4.655575	1.279326
N	−1.424076	−4.102812	0.506273
C	−0.366944	−4.976720	0.056181
H	0.018521	−5.582947	0.899852
H	−0.821290	−5.648627	−0.698367
C	−1.277649	−3.158891	1.615700
H	−0.410924	−2.491102	1.430836
N	−1.196231	−3.740219	2.930921
C	0.071967	−3.941908	3.612967
H	−0.144527	−4.440372	4.575764
H	0.575731	−2.971009	3.823691
H	0.753070	−4.566115	3.005297
C	−2.352630	−3.484242	3.678843
O	−2.542163	−3.798435	4.846605
N	−3.236751	−2.784650	2.863888
C	−4.514545	−2.306072	3.345414
H	−4.487839	−2.316839	4.452619
H	−4.703603	−1.280481	2.972224

H	−5.356945	−2.952718	3.011777
C	−2.648793	−2.400399	1.602385
H	−2.538410	−1.293879	1.533405
N	−3.310285	−2.905712	0.410442
C	−2.570223	−3.882394	−0.242566
O	−2.876415	−4.443525	−1.295837
N	−4.284271	−0.954755	−0.633115
C	−4.495866	−2.305130	−0.165764
H	−5.311663	−2.248988	0.581680
H	−4.805775	−2.964468	−0.999995
C	−3.336120	−0.615021	−1.694052
H	−2.340682	−1.054340	−1.462657
N	−3.736976	−0.953625	−3.033599
C	−3.321493	−2.179657	−3.688095
H	−3.711443	−3.074758	−3.168071
H	−2.209790	−2.259881	−3.723955
H	−3.708304	−2.143693	−4.723238
C	−4.049758	0.187397	−3.782858
O	−4.347678	0.211877	−4.970490
N	−3.936669	1.288334	−2.939507
C	−4.062957	2.645864	−3.423566
H	−5.025120	3.111838	−3.113237
H	−3.240878	3.273416	−3.022654
H	−4.031095	2.619747	−4.530509
C	−3.341271	0.949910	−1.667111
H	−2.323758	1.392122	−1.578348
N	−4.117314	1.272430	−0.482779
C	−4.641984	0.147020	0.134681
O	−5.300885	0.127413	1.175177
N	−2.856211	3.032374	0.604688
C	−4.142272	2.586583	0.131429
H	−4.865270	2.524467	0.969103
H	−4.485248	3.348466	−0.595633
C	−2.148628	2.457597	1.754914
H	−1.923558	1.386582	1.573592
N	−2.786827	2.627361	3.031734
C	−3.531521	1.553830	3.668714
H	−3.825241	1.911776	4.672516
H	−2.899325	0.644316	3.785532
H	−4.433235	1.284315	3.086062
C	−2.127701	3.593607	3.808907
O	−2.411083	3.911696	4.955202
N	−1.083409	4.107426	3.043759
C	−0.091260	4.999248	3.605057
H	−0.221940	5.011374	4.705028
H	0.928102	4.639712	3.353143
H	−0.200155	6.039746	3.225271
C	−0.866227	3.349245	1.832865
H	0.079708	2.764513	1.891973
N	−0.902699	4.114610	0.599611
C	−2.082821	3.937954	−0.106245
O	−2.381511	4.481335	−1.171176
N	1.287483	4.137709	−0.431586
C	0.195092	4.915208	0.107197
H	0.621334	5.531066	0.922147
H	−0.220986	5.578340	−0.675617
C	1.153924	3.297432	−1.617602
H	0.254246	2.650366	−1.515974
N	1.136506	3.977266	−2.888310
C	−0.099694	4.337359	−3.556739
H	−0.656015	5.119568	−3.006949
H	−0.770143	3.453453	−3.663042

H	0.171246	4.703326	−4.564605
C	2.285959	3.699342	−3.638624
O	2.498773	4.052243	−4.792102
N	3.129848	2.925394	−2.848023
C	4.337498	2.325553	−3.373333
H	5.254381	2.830546	−2.996386
H	4.393434	1.258433	−3.076069
H	4.316321	2.423011	−4.476518
C	2.497087	2.491876	−1.625279
H	2.350001	1.388098	−1.630069
N	3.141986	2.887917	−0.386702
C	2.385300	3.791762	0.347089
O	2.638262	4.207226	1.477831
Cl	−0.129119	−0.248699	2.593587
I	0.047207	0.037907	−0.138444
I	0.035970	0.092799	−3.025674
I	1.829588	3.119618	6.677663
I	0.864082	1.487505	4.636197

7 Author Contributions

Cicolani and Demets conceived the study and analyzed the data. Batista and Oliveira-Filho realized and analyzed all theoretical calculations. All the authors have helped to write the present communication.

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