Electronic Supplementary Information for

A combined spectroscopic and computational investigation on dispersion-controlled docking of Ar atoms on 2-(2'-pyridyl) benzimidazole

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SI Table T1: The experimental band positions (ν_{expt}) and vibrational frequencies in the ground (ν''_{Expt}) and excited (ν'_{Expt}) states of the PBI-Ar cluster are listed along with the possible assignments. The calculated ground (ν'') and excited (ν') state frequencies are scaled using 0.983 and 0.9345 factors, respectively.

R2PI spectrum of PBI-Ar				**SVLF spectrum of PBI-Ar**			
ν_{Expt} (cm^{-1})	ν'_{Expt} (cm^{-1})	**Band**	ν'_{Calc} (cm^{-1})	ν_{Expt} (cm^{-1})	ν''_{Expt} (cm^{-1})	**Band**	ν''_{Calc} (cm^{-1})
31571	0	0_0^1	0	31571	0	0_0^1	0
31580	9	X_0^1	11	31677	105	45_1^0	106
31595	24	Y_0^1	31	31783	212	45_2^0	212
31612	40	Z_0^1	44	31864	292	44_1^0	299
31651	80	65_0^1	86	31889	317	45_3^0	318
31663	92	45_0^1	91	31976	404	$45_1^0 44_1^0$	404
31672	101	$45_0^1 X_0^1$	103	31994	423	45_4^0	423
31681	110	$45_0^1 Y_0^1$	123	32074	503	42_1^0	546
31704	132	$45_0^1 Z_0^1$	135	32189	618	39_1^0	644
31755	183	45_0^2	183	32298	726	38_1^0	726
31764	193	$45_0^2 X_0^1$	194				
31779	207	$45_0^2 Y_0^1$	214				
31795	224	$45_0^2 Z_0^1$	227				
31847	275	45_0^3	274				
31879	307	43_0^1	315				
31887	316	$45_0^3 Z_0^1$	318				
31903	331						
31939	367	45_0^4	365				
31992	420						
32001	429						
32011	440						
32031	460	45_0^5	457				

32040	469	42_0^1	466				

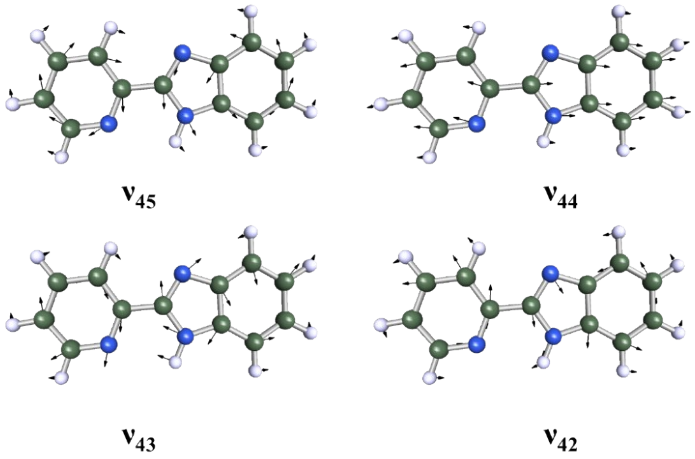
SI Table T2: Calculated binding energies with (D_0) and without (D_e) zero-point vibrational energy correction in the ground (S_0) are given in kJ/mol. Structures optimized at MP2 level of theory using aug-cc-pVDZ basis set. The counterpoise (CP) corrections were applied on the optimized geometry.

Structures	**0% CP corrected**		**100% CP corrected**	
	$D_e(S_0)$	**$D_0(S_0)$**	**$D_e(S_0)$**	**$D_0(S_0)$**
PBI-Ar-1	13.7	-	7.2	-
PBI-Ar-2	10.9	-	5.9	-
PBI-Ar_2-1	27.7	26	14.4	12.7
PBI-Ar_2-2	25.6	23.9	13.6	11.9

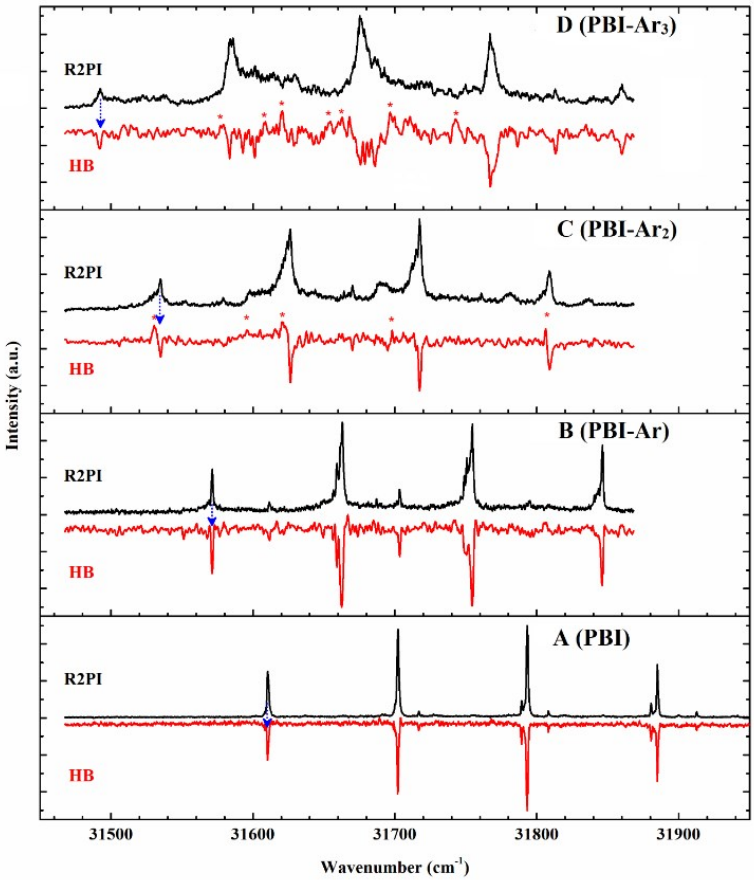
Note: The MP2 level optimized geometry of PBI-Ar_2 isomers 1 & 2 were used to calculate single point CCSD(T) energies. The isomers were found to be separated by 2 kJ/mol, with isomer 1 being more stable.

SI Table T3: Low frequency intermolecular vibrational frequencies in cm^{-1} ν_X, ν_Y and ν_Z of PBI-Ar_n isomers in the S_1 state are listed. The frequencies are scaled with 0.9345 to compare with the experimental data.

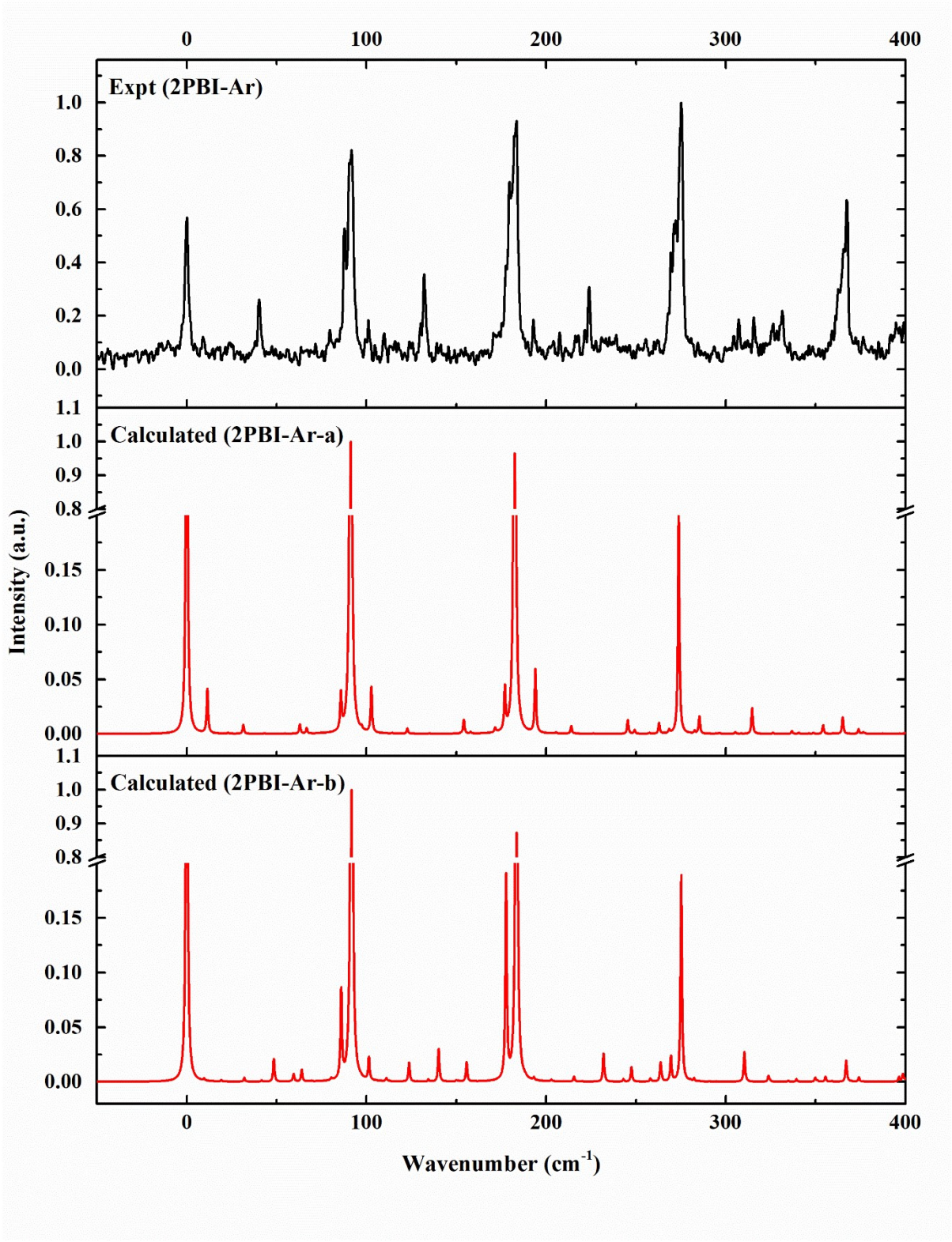
Mode	**2PBI-Ar_1**	**2PBI-Ar_2**			**Expt**
ν_X	11	10			9
ν_Y	31	32			24
ν_Z	44	49			40
Mode	**2PBI-Ar2_1**	**2PBI-Ar2_2**	**2PBI-Ar2_3**	**2PBI-Ar2_4**	
ν_X	10	15	11	11	
ν_Y	16	35	14	17	18
ν_Z	46	51	48	52	44
Mode	**2PBI-Ar3_1**	**2PBI-Ar3_2**	**2PBI-Ar3_3**		
ν_X	12	8	1		
ν_Y	15	17	29		
ν_Z	51	53	52		46



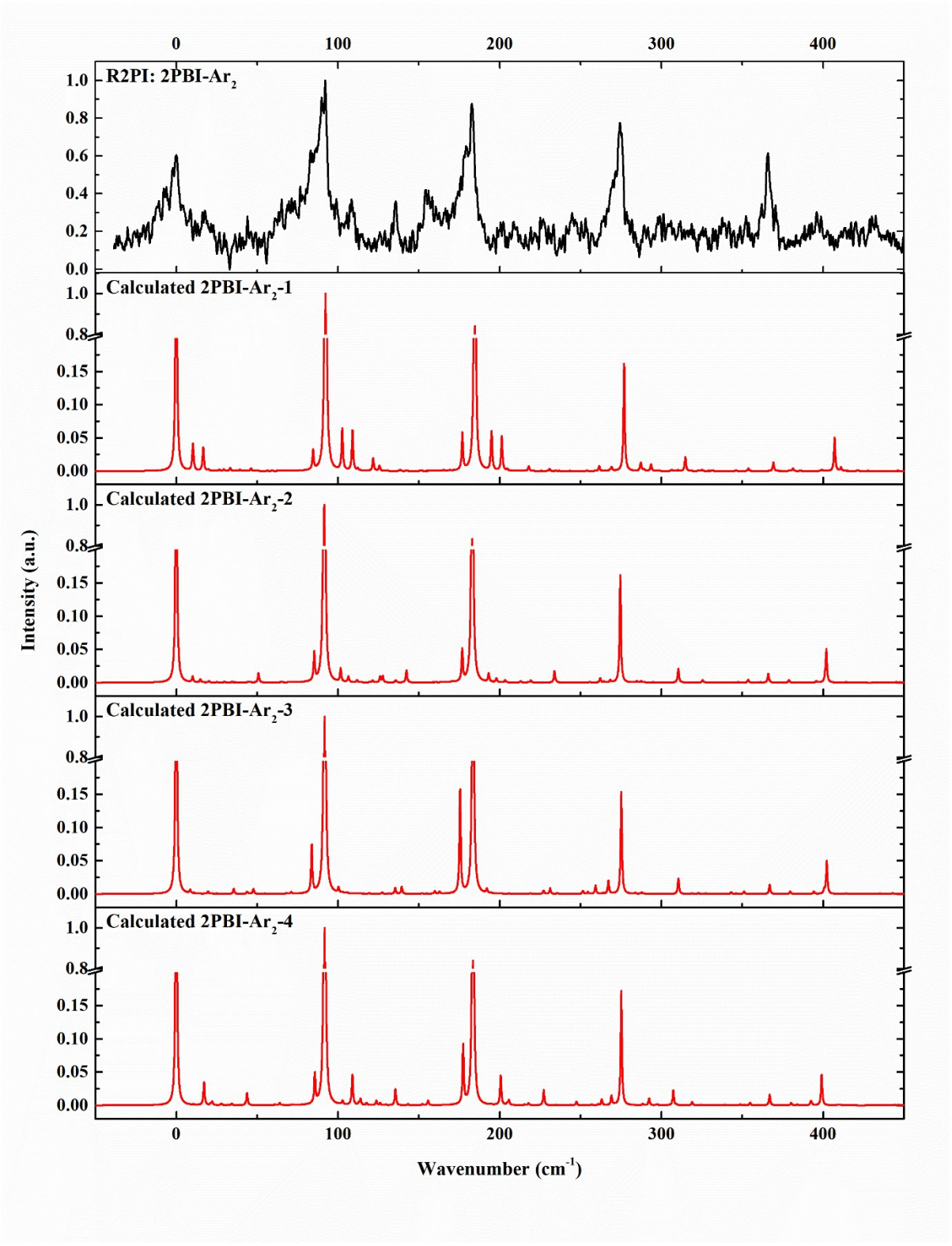
SI Figure S1: Vibrational modes of the first four lowest energy totally symmetric (a') vibrational modes of PBI molecules. The arrows indicate the bending (ν_{45}), twisting (ν_{43}, ν_{42}) and stretching (ν_{44}) motions with respect to the C-C linkage between the pyridyl and imidazolyl groups. Identical motions are present in the PBI-Ar_n complexes in both the ground and excited states.



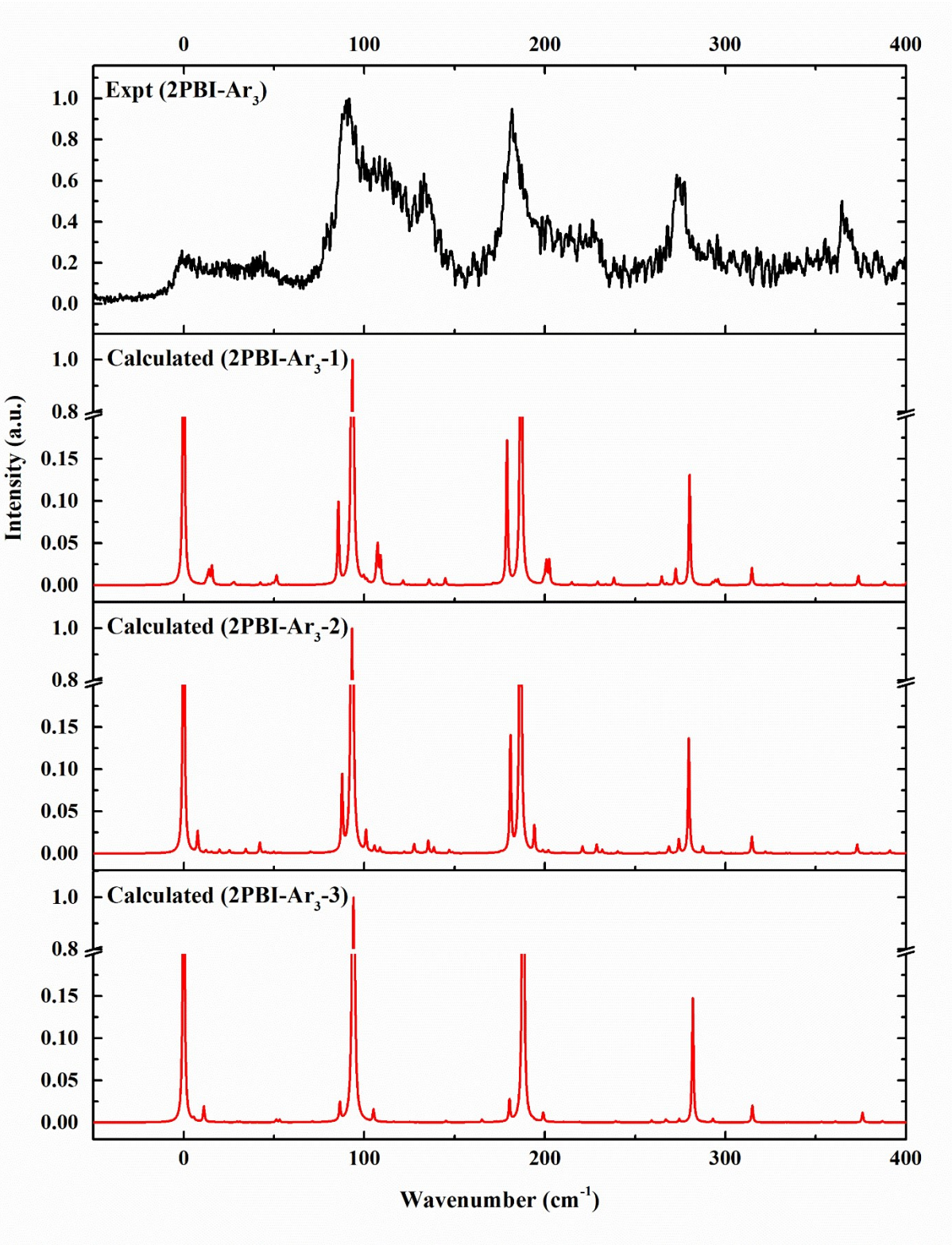
SI Figure S2. The difference spectra (HB) of PBI-Ar_n complexes were recorded by subtracting the R2PI spectra recorded with and without the hole-burning laser. The dotted arrows indicate the wavenumbers of the hole-burning laser positions. The * indicates contributions from low energy isomers in the PBI-$Ar_{2/3}$ systems.



SI Figure S3: Comparison of the FC simulation spectrum with the experimental spectrum recorded for PBI-Ar system.



SI Figure S4: Comparison of the FC simulation spectrum with the experimental spectrum recorded for PBI-Ar2 system.



SI Figure S5: Comparison of the FC simulation spectrum with the experimental spectrum recorded for PBI-Ar_3 system.

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SI Table T4: Coordinates of the optimized structures of PBI and its complexes with Ar atoms, calculated using B3LYP-D3(BJ)/def2-TZVPP.

PBI-N(S_0)				PBI-N(S_1)			
Atom	X	Y	Z	Atom	X	Y	Z
C	-2.439	1.35	0.0	C	-2.4628	1.3677	0.0
H	5.1467	0.9999	0.0	H	5.1934	0.9593	0.0
N	-2.3481	-1.0529	0.0	N	-2.319	-1.0833	0.0
H	5.0286	-1.4539	0.0	H	5.017	-1.4931	0.0
H	-5.5394	-0.0031	0.0	H	-5.5298	-0.074	0.0
C	-3.8227	1.3084	0.0	C	-3.8402	1.3061	0.0
C	1.7469	-0.768	0.0	C	1.7316	-0.7539	0.0
H	2.8503	-2.6329	0.0	H	2.7907	-2.6224	0.0
N	0.4047	-1.0682	0.0	N	0.3712	-1.0237	0.0
C	3.0314	1.2997	0.0	C	3.0718	1.2964	0.0
C	4.1101	-0.8826	0.0	C	4.1224	-0.8872	0.0
N	0.516	1.1656	0.0	N	0.572	1.2216	0.0
C	-1.7397	0.1418	0.0	C	-1.7267	0.1701	0.0
C	-4.4612	0.0729	0.0	C	-4.4548	0.033	0.0
C	2.8959	-1.5523	0.0	C	2.8469	-1.5426	0.0
C	-0.28	0.1203	0.0	C	-0.3004	0.1559	0.0
H	-0.0485	-1.9662	0.0	H	-0.13	-1.9008	0.0
H	-4.1406	-2.0559	0.0	H	-4.101	-2.0871	0.0
C	1.7965	0.6483	0.0	C	1.8001	0.672	0.0
H	-4.3973	2.225	0.0	H	-4.4328	2.2099	0.0
H	-1.8875	2.2783	0.0	H	-1.9338	2.3106	0.0
C	4.1767	0.5215	0.0	C	4.2183	0.4934	0.0
H	3.0788	2.3797	0.0	H	3.137	2.3753	0.0
C	-3.6784	-1.0755	0.0	C	-3.641	-1.1032	0.0

Table T4: Continues

PBI-Ar-a				PBI-Ar-b				PBI-Ar_2-a			
Atom	X	Y	Z	Atom	X	Y	Z	Atom	X	Y	Z
H	-5.4243	0.1208	0.4306	H	-5.4467	0.1281	0.3524	H	-5.4115	0.1235	0.383
C	-3.5932	-0.9922	0.2849	C	-3.6142	-0.9858	0.2368	C	-3.5775	-0.9883	0.2683
C	-1.638	0.1817	0.0874	C	-1.6561	0.187	0.0679	C	-1.6194	0.1873	0.1152
H	0.0053	-1.9613	0.0037	H	-0.013	-1.9573	0.0147	H	0.0244	-1.9547	0.029
H	3.2115	2.3154	-0.2966	H	3.1976	2.3166	-0.2909	H	3.23	2.3234	-0.2531
H	5.0808	-1.558	-0.3255	H	5.0638	-1.5583	-0.3189	H	5.0974	-1.5503	-0.3315
C	3.1425	1.2368	-0.2724	C	3.128	1.2382	-0.2605	C	3.1611	1.2447	-0.2336
C	4.1755	-0.9675	-0.2864	C	4.1592	-0.9669	-0.2745	C	4.1929	-0.9598	-0.2761
C	-0.1846	0.1285	-0.0334	C	-0.2005	0.133	-0.0241	C	-0.1648	0.1353	0.0136
C	1.8191	-0.8027	-0.1532	C	1.8037	-0.7999	-0.1273	C	1.8386	-0.7952	-0.1137
N	0.4743	-1.0739	-0.0594	N	0.4581	-1.0701	-0.0361	N	0.4944	-1.0667	-0.0165
C	-2.3098	1.4049	0.1244	C	-2.3279	1.4102	0.0883	C	-2.2921	1.4101	0.1469
C	4.2701	0.4346	-0.321	C	4.2547	0.435	-0.314	C	4.2877	0.4426	-0.3015
N	-2.2681	-0.999	0.1658	N	-2.2875	-0.9933	0.1385	N	-2.2503	-0.9941	0.175
C	-4.3492	0.173	0.3318	C	-4.3703	0.1797	0.2688	C	-4.3347	0.1765	0.3066
H	-4.2419	2.3228	0.2818	H	-4.2617	2.3291	0.2123	H	-4.2272	2.3266	0.2714
H	5.248	0.8922	-0.3861	H	5.2323	0.8916	-0.388	H	5.2648	0.9002	-0.3758
H	-1.7414	2.3205	0.0571	H	-1.7582	2.3255	0.0281	H	-1.7227	2.326	0.0951
N	0.6303	1.1563	-0.1109	N	0.6155	1.1601	-0.0994	N	0.6501	1.1634	-0.057
C	1.8971	0.6119	-0.1864	C	1.8824	0.6146	-0.1661	C	1.9166	0.6196	-0.1381
C	2.9501	-1.611	-0.2023	C	2.9339	-1.6093	-0.1802	C	2.9684	-1.6035	-0.182
C	-3.6884	1.3939	0.2489	C	-3.7081	1.4	0.191	C	-3.6728	1.3981	0.2443
H	-4.0733	-1.9621	0.3465	H	-4.0955	-1.9553	0.2942	H	-4.0585	-1.9586	0.3147
H	2.8829	-2.6901	-0.174	H	2.8661	-2.6883	-0.1505	H	2.9009	-2.6827	-0.1629
Ar	1.0298	-0.0704	3.2776	Ar	-2.1603	0.0711	3.5702	Ar	1.027	-0.0954	3.3281
								Ar	0.5769	-0.1883	-3.4279

Table T4: Continues

PBI-Ar_2-b				PBI-Ar_2-c				PBI-Ar_2-d			
Atom	X	Y	Z	Atom	X	Y	Z	Atom	X	Y	Z
H	-5.4592	0.1104	0.3376	H	-5.495	0.139	5.0E-4	H	-5.4833	0.1356	0.4305
C	-3.6253	-1.0	0.2111	C	-3.6584	-0.9743	0.0063	C	-3.6513	-0.9788	0.3118
C	-1.6681	0.1769	0.0597	C	-1.694	0.1992	-0.0352	C	-1.6939	0.1935	0.1374
H	-0.0222	-1.9645	-0.0199	H	-0.0512	-1.944	0.0213	H	-0.0554	-1.952	0.0542
H	3.1842	2.3166	-0.2474	H	3.1719	2.3279	-0.1322	H	3.1577	2.3183	-0.2738
H	5.0561	-1.5553	-0.2972	H	5.0354	-1.5474	-0.0439	H	5.0177	-1.5591	-0.3393
C	3.1157	1.2378	-0.2342	C	3.1005	1.2497	-0.0969	C	3.0869	1.2399	-0.2474
C	4.1501	-0.9657	-0.2602	C	4.13	-0.9557	-0.0471	C	4.1146	-0.9666	-0.2823
C	-0.2128	0.1257	-0.0359	C	-0.236	0.1456	-0.0322	C	-0.2401	0.1384	0.0272
C	1.7927	-0.8034	-0.146	C	1.7704	-0.7874	-0.0166	C	1.7612	-0.7969	-0.1069
N	0.4473	-1.0762	-0.0651	N	0.4222	-1.0569	0.0036	N	0.4166	-1.0654	7.0E-4
C	-2.3412	1.3991	0.097	C	-2.3661	1.4221	-0.0617	C	-2.3647	1.4169	0.1642
C	4.2442	0.4367	-0.2809	C	4.228	0.446	-0.09	C	4.2117	0.4353	-0.317
N	-2.2985	-1.0049	0.1146	N	-2.3283	-0.9813	-0.0046	N	-2.3252	-0.9864	0.2098
C	-4.3827	0.1642	0.2568	C	-4.4155	0.1909	-0.0126	C	-4.407	0.1869	0.3464
H	-4.2761	2.3142	0.231	H	-4.3043	2.3403	-0.0651	H	-4.2978	2.3363	0.2944
H	5.2222	0.8954	-0.3336	H	5.2084	0.902	-0.1189	H	5.1891	0.8908	-0.4001
H	-1.7723	2.3156	0.0502	H	-1.794	2.3375	-0.0864	H	-1.7949	2.3319	0.1017
N	0.6023	1.1546	-0.0958	N	0.5831	1.1725	-0.0669	N	0.5763	1.1647	-0.055
C	1.87	0.6115	-0.1652	C	1.8516	0.6268	-0.0598	C	1.8416	0.6177	-0.1406
C	2.9244	-1.6106	-0.1925	C	2.9013	-1.5972	-0.0097	C	2.8895	-1.6076	-0.1768
C	-3.7216	1.3861	0.1973	C	-3.7501	1.4114	-0.049	C	-3.7445	1.4071	0.2706
H	-4.1058	-1.9706	0.2556	H	-4.1422	-1.9439	0.033	H	-4.133	-1.9481	0.3685
H	2.8577	-2.6899	-0.1744	H	2.8315	-2.676	0.0214	H	2.8205	-2.6866	-0.1505
Ar	1.2579	-0.1135	3.2768	Ar	0.7155	-0.2247	-3.4117	Ar	-2.1978	0.0803	3.6441
Ar	-2.4594	0.0494	3.5819	Ar	-2.4049	0.0773	3.4258	Ar	-2.7305	-0.0591	-3.2436

Table T4: Continues

PBI-Ar_3-a				PBI-Ar_3-b				PBI-Ar_3-c			
Atom	X	Y	Z	Atom	X	Y	Z	Atom	X	Y	Z
H	-5.5795	0.1708	0.6196	H	-5.596	0.1617	0.7382	H	-5.5923	0.1489	-0.1209
C	-3.7597	-0.9538	0.4309	C	-3.7763	-0.961	0.5379	C	-3.7599	-0.9703	-0.1639
C	-1.8047	0.2071	0.1702	C	-1.83	0.2007	0.224	C	-1.7908	0.1963	-0.1491
H	-0.1791	-1.9462	0.0404	H	-0.2037	-1.9514	0.0873	H	-0.1541	-1.9529	-0.2117
H	3.0343	2.3064	-0.4569	H	2.994	2.3008	-0.5086	H	3.0831	2.3105	-0.1253
H	4.8736	-1.5799	-0.5641	H	4.8414	-1.5824	-0.5814	H	4.9339	-1.5697	-0.2309
C	2.96	1.2285	-0.4188	C	2.9223	1.2233	-0.4579	C	3.0081	1.2324	-0.1539
C	3.976	-0.9829	-0.4759	C	3.9431	-0.9864	-0.4949	C	4.0304	-0.9755	-0.2155
C	-0.3564	0.1445	0.0059	C	-0.3862	0.1383	0.0235	C	-0.3326	0.1378	-0.1629
C	1.633	-0.8008	-0.206	C	1.6015	-0.8061	-0.2097	C	1.6711	-0.8012	-0.1983
N	0.2938	-1.062	-0.0369	N	0.265	-1.0679	-0.0198	N	0.3218	-1.0669	-0.1989
C	-2.4682	1.4342	0.2151	C	-2.4953	1.4267	0.2658	C	-2.4585	1.4214	-0.1112
C	4.0776	0.4182	-0.5274	C	4.0409	0.4142	-0.5647	C	4.1328	0.4258	-0.1817
N	-2.4387	-0.9693	0.2747	N	-2.4584	-0.9753	0.3591	N	-2.4297	-0.9819	-0.1742
C	-4.5075	0.216	0.4896	C	-4.5262	0.2076	0.591	C	-4.5126	0.1973	-0.129
H	-4.3899	2.3645	0.419	H	-4.4154	2.3551	0.4892	H	-4.3932	2.346	-0.0717
H	5.0527	0.8684	-0.6547	H	5.0142	0.865	-0.7041	H	5.1147	0.8789	-0.1728
H	-1.8966	2.3458	0.125	H	-1.928	2.3382	0.1513	H	-1.883	2.3347	-0.0897
N	0.4601	1.1662	-0.1201	N	0.4261	1.1599	-0.1288	N	0.49	1.1622	-0.1417
C	1.7179	0.6129	-0.2556	C	1.6829	0.6071	-0.277	C	1.7569	0.6129	-0.163
C	2.7536	-1.6172	-0.3144	C	2.7234	-1.6214	-0.3163	C	2.7998	-1.614	-0.2231
C	-3.8427	1.4322	0.3779	C	-3.8665	1.4237	0.4522	C	-3.8426	1.4154	-0.1017
H	-4.2433	-1.9203	0.5147	H	-4.2558	-1.9273	0.6438	H	-4.2474	-1.9382	-0.183
H	2.6811	-2.6955	-0.2743	H	2.6539	-2.6992	-0.2606	H	2.7267	-2.6927	-0.2468
Ar	-2.4189	0.1394	3.7234	Ar	-2.3908	0.1783	3.7937	Ar	4.2331	-0.3492	3.3904
Ar	0.1708	-0.2334	-3.4572	Ar	-3.0174	-0.1467	-3.0883	Ar	0.5763	-0.2474	3.2096
Ar	1.2801	-0.0329	3.2347	Ar	1.2968	-0.0149	3.2238	Ar	-3.0932	-0.0039	3.327