ADVANCED ELECTRONIC MATERIALS

Supporting Information

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Addressing the Elusive Polaronic Nature of Multiple Redox States in a #-Conjugated Ladder-Type Polymer

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Supporting Information

Addressing the elusive polaronic nature of multiple redox states in a □-conjugated ladder-type polymer.

Daniele Fazzi,[1] Fabrizia Negri*[2]

COMPUTATIONAL DETAILS

All calculations were performed via an oligomer approach. Oligomers from length n = 1 to 8 were considered. Each structure was optimized by using the hybrid range-separated-corrected DFT functional, namely ωB97X-D combined with double-zeta (and in some cases triple-zeta) split valence polarized Pope's basis set 6-31G* (6-311G*). The choice of ωB97X-D was due to its well-known superior performance in describing charged and excited states in conjugated polymers.[1-3] The effects of considering either B3LYP or a double hybrid DFT functional (e.g., B2PLYP), as well as an augmented basis set (e.g., 6-311+G*), were tested previously.[4] Results did not show improvements with respect to ωB97X-D/6-31G* approach, and similar conclusion regarding the DFT instability in describing charged states can be drawn.

The electronic states investigated here were the neutral ground (q = 0e), the single negatively/positively charged states (q = ±1e), and the double negatively/positively charged (q = ±2e) states. Such states are referred to as polaron and bipolaron. A polaron shows a doublet state spin multiplicity (D), while a bipolaron can be either a singlet (S) or a triplet (T) state. Polarons were initially described using the UDFT approach, whereas for bipolarons the singlet was described using the RDFT and triplet the UDFT approaches. For each case, a wavefunction stability check was run using the BS-UDFT scheme. The BS scheme can be computed directly in Gaussian16 code by running a single-point calculations combining the

keywords `guess=mix` and `stable=opt`. In ORCA code, a similar approach is introduced by using the following keywords for the %scf block (a general example below):

```
%scf
 guess hcore
 HFTyp UHF
 STABPerform true
 STABRestartUHFifUnstable true
 STABNRoots 3
 STABMaxDim 3
 STABMaxIter 500
end
```

If an instability in the wavefunction was found, both the electronic and nuclear structures were re-optimized following the BS-UDFT potential energy surface (namely, by restarting the calculation with the BS wavefunction obtained in the previous step (guess=read in Gaussian or MORead keyword in ORCA). All calculations were performed with the program package Gaussian16 B.01[5] and ORCA v4.2.0.

Extra (multiple) charged states were investigated, namely q = 3e$^-$ and q = 4 e$^-$. Such states are characterized by different state multiplicities, namely quartet (Q) and doublet (D) for q = 3e$^-$, and quintet (Qui), triplet (T) and singlet (S) for q = 4e$^-$. For each state, broken-symmetry stability check for the DFT wavefunction was performed.

In general, we considered (for each oligomer length) a variety of multiple charged states, encompassing polaron, bipolaron or extra charges up to one charge per repeat unit (depending on the oligomer length).

Specifically, we considered the following charged cases:

- BBL1: q= 0, ±1, ±2
- BBL2: q= 0, ±1, ±2
- BBL3: q= 0, ±1, ±2, -3
- BBL4: q= 0, ±1, ±2, -3, -4
- BBL5: q= 0, ±1, ±2, -3, -4, -5
- BBL6-8: q=0, ±1, ±2

Focus of the computational investigation was the modelling of hole/electron polaron (±1), bipolaron (±2) for all BBL oligomers, and multiple charged (i.e., negative) states for some of them, specifically for BBL4 considered to be the reference model system (as discussed in the main text) for the interpretation of the experimental spectro-electrochemical data.
FOD and CASSCF/NEVPT2 calculations (with def2-TZVP basis set) were performed by using ORCA v 4.2.0.

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Molecular Orbital (MO) analysis for BBL1-4.

In **Figure S1** are reported the MO energies for BBL1-4, together with the computed HOMO/HOMO-1 and LUMO/LUMO+1 gaps (in eV, see inset) and the FOD number (N_{FOD}). Calculations refer to ωB96X-D/6-31G* data.

FOD calculations (**Table S1**) were performed by using the standard (as implemented in ORCA) TPSS functional, or ωB96X-D with def2-SVP and/or def2-TZVP, both leading to similar results.

Table S1. FOD numbers (N_{FOD}) of neutral, electron/hole polarons (P±(D)) and bipolarons B±(S) **BBL** *cis* and *trans* oligomers (n=1,4). A label (*) identified those species where a BS-UDFT solution was found.

		N_{FOD}				
BBL**N**		**N (S)**	**P+ (D)**	**P- (D)**	**B+ (S)**	**B- (S)**
1	*cis*	0.6835	1.507	0.768	2.153*	0.867
	trans	0.6628	1.630	0.763	2.483*	0.869
2	*cis*	1.339	2.275	1.879*	3.136*	2.389*
	trans	1.307	2.235	1.749*	3.284*	2.170*
3	*cis*	1.993	2.970	2.631	3.869*	3.213*
	trans	1.950	2.900*	2.509	3.804*	3.053*
4	*cis*	2.640	3.622	3.329*	4.538*	4.029*
	trans	2.593	3.547	3.206*	4.470*	3.808*

The analysis of the molecular orbitals (MOs) revealed an increase number of *quasi*-degenerate levels the longer is the oligomer chain, together with a high number of occupied MOs with fractional occupations between 0.3 and 1.98 (see Figure S1 and Figure S2 Supporting Information).

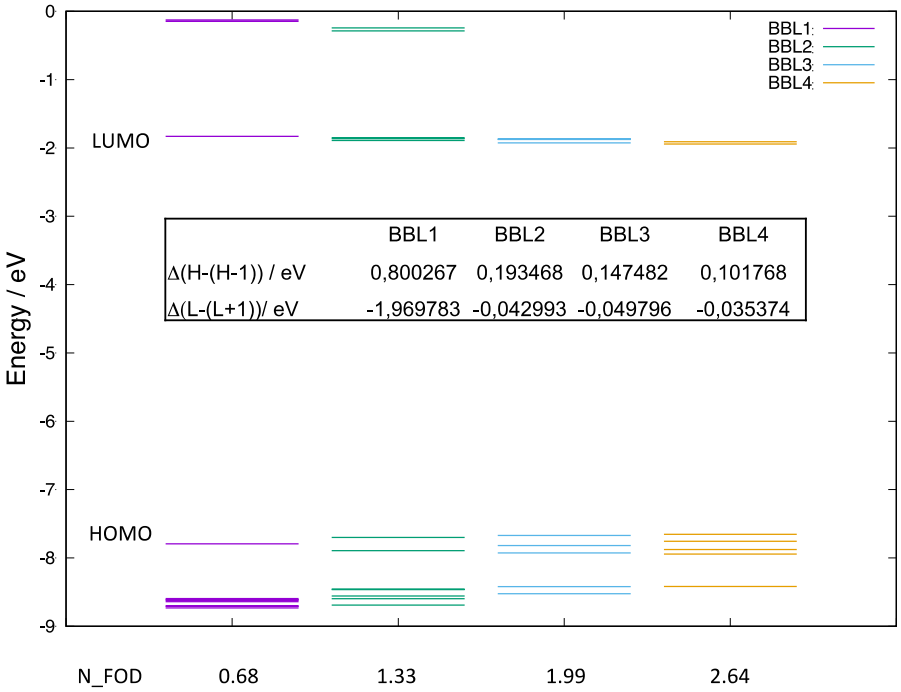


Figure S1

In **Figure S2** are reported the MOs (ωB96X-D/6-31G*) for BBL4 *cis* neutral.

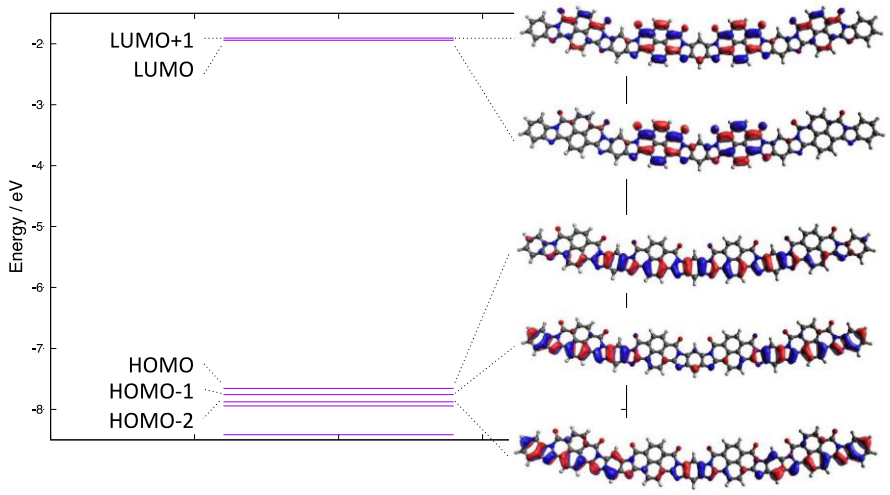


Figure S2

List of frontier MOs and respective fractional occupation number for BBL4 *cis* neutral species, as computed in the FOD analysis.

```
  NO   OCC
...
 340   1.9864
 341   1.9853
 342   1.9848
 343   1.9846
 344   1.9842
 345   1.9838
 346   1.9835
 347   1.9833
 348   1.9832
 349   1.9830
 350   1.9826
 351   1.9637
 352   1.9611
 353   1.9555
 354   1.9492
 355   1.9357
 356   1.9279
 357   1.8510
 358   1.8386
 359   1.8035
 360   1.7611  # HOMO
 361   0.3312  # LUMO
 362   0.3128
 363   0.2939
 364   0.2840
 365   0.0249
 366   0.0182
 367   0.0112
 368   0.0065
 369   0.0062
 370   0.0054
 371   0.0041
 372   0.0038
 373   0.0033
 374   0.0033
 375   0.0033
 376   0.0033
 377   0.0020
      …
```

DETAILS OF THE CASSCF/NEVPT2 CALCULATIONS PERFORMED ON BBL1

BBL1 shows stable DFT solutions for the neutral, singly charged P±(D) and electron doubly charged B-(S) states, however a DFT instability was found for the hole bipolaron B+(S) state, leading to a BS-UDFT ground state (**Figure 1** main text). Accordingly, the FOD analysis highlights a weak MR character for the neutral (N, N_{FOD} < 0.7) and electron charged (P- and B-, N_{FOD} < 0.8) species (Table 1 main text), while higher MR characters are predicted for the positive charged states, both polaron (P+, N_{FOD} >1.5) and, especially, bipolaron (B+, N_{FOD} >2.0).

We performed CASSCF/NEVPT2 calculations (see Supporting Information) for both electron and hole bipolarons (B-(S) and B+(S)) to clearly address the presence (or not) of MR characters, therefore to correlate such aspects with the appearance (or not) of BS-UDFT solutions. CASSCF wavefunction for BBL1 B+(S) undoubtedly indicate a strong contribution of doubly excited determinants (i.e., H,H -> L,L - with H the highest occupied molecular orbital and L lowest one) in the description of the ground state (~40%), highlighting its pronounced MR character. For such state a low energy BS-UDFT solution was indeed found (**Figure 1** main text). On the contrary, the CASSCF wavefunction for the electron bipolaron B-(S) revealed only negligible contributions (< 9%) of doubly excited configurations to the ground state. The latter was found stable at the DFT level, without reporting any BS-UDFT solution (**Figure 1** main text).

***trans*, BIPOLARON (q = ±2e).**

Hole bipolaron (q=+2e) species

CASSCF/NEVPT2 with def2-TZVP basis set on top of DFT BS geometry.

CAS space: (10,12) - 10 electrons in 12 orbitals.

Ground state wavefunction composition highlighting the HOMO/LUMO orbitals and the doubly excited determinant.

ROOT 0:
0.46762: 2222**20**000000
0.37514: 222202000000
0.01928: 212221000000
0.00892: 222112000000
0.00875: 212211100000
0.00670: 112220100100
0.00592: 221120011000
0.00586: 221211001000
0.00580: 222111010000
0.00473: 221102011000
0.00439: 112202100100
0.00415: 022220000200
0.00412: 202220200000
0.00332: 022202000200
0.00257: 202202200000

Electron bipolaron (q=-2e) species

CASSCF/NEVPT2 with def2-TZVP basis set on top of DFT geometry.

CAS space: (8,9)

Ground state wavefunction composition highlighting the HOMO/LUMO orbitals and the doubly excited determinant.

ROOT 0:
0.95322: 222**20**0000
0.01376: 222020000
0.00719: 212111000
0.00447: 221110100
0.00366: 222002000

IR SPECTROSCOPIC ASSIGNMENTS

Experimental FT-IR data are taken from T. Yohannes et al., *J. Phys. Chem.* B **2000,** 104, 9430-9437.

Computed frequencies (scaled values are reported, scale factor 0.93, level of theory ωB97X-D/6-31G*) refer to BBL4 *cis*.

Neutral species

ν expt. cm^{-1}	ν theo. cm^{-1}	Assignment
1703	1711-1705 (six active IR normal modes)	CO asymmetric stretching
1500	1543	CC str. + CN str.
1370	1388	CH rocking
1320	1321	quinoidal mode on benzimidazole + CN str.
1237	1275	quinoidal mode on benzimidazole + CN str.
1171	1171	CH rocking

Charged speciesSpecies A, q = 1e- (0.25eru)

Computed values refer to the BS-UDFT geometry (polaron P-, D-BS state).

ν expt. cm^{-1}	ν theo. cm^{-1}	Assignment
1649	1640	CO asymmetric stretching localized on one benzophenantroline unit (polaron localisation)
1522	1503	quinoidal mode on benzophenantroline + CN str.
1255	1273	CH rocking + CN str.
1150	1170	quinoidal mode on benzimidazole + CN str.

Charged species

Species B, q = 2e- (0.50eru)

Computed values refer to the BS-UDFT geometry (bipolaron B-, S-BS state).

ν expt. cm^{-1}	ν theo. cm^{-1}	Assignment
1614	1635	CO asymmetric stretching localized on two units (bipolaron localisation)
not reported	1501	quinoidal mode on benzophenantroline + CN str.
1278	1272	quinoidal mode on benzimidazole + CN str.
1219	1241	
1099	1169	CH rocking + CN str.
1028		*spurious bands associated to a protonated species (see manuscript)*

Charged species

Species C, q = 3e- (0.75eru)

Computed values refer to the BS-UDFT geometry (Quartet, Q-BS state).

ν expt. cm^{-1}	ν theo. cm^{-1}	Assignment
not reported	1627	CO asymmetric stretching localized on one unit
1509	1500	quinoidal mode on benzophenantroline + CN str.
1369	1360	CH rocking on benzimidazole + CN str. + quinoidal mode on benzophenantroline
1070	1169	CH rocking on benzophenantroline

Charged species

Species D, q = 4e- (1eru)

Computed values refer to the UDFT geometry (Quintet, Qui).

ν expt. cm^{-1}	ν theo. cm^{-1}	Assignment
1593	1620	CO asymmetric stretching localized on two units
not reported	1469	quinoidal mode on benzophenantroline + CN str.
1363	1359	CH rocking on benzimidazole + CN str.
not reported	1170	CH rocking on benzophenantroline

COMPUTED IR SPECTRA FOR EACH STATE SPIN MULTIPLICITIES

Computed IR spectra (ω□□□□□□□□□□□□□□□□belonging to the same charged state but differing for their spin multiplicity. Differences are almost imperceptible and IR spectra basically overlap.

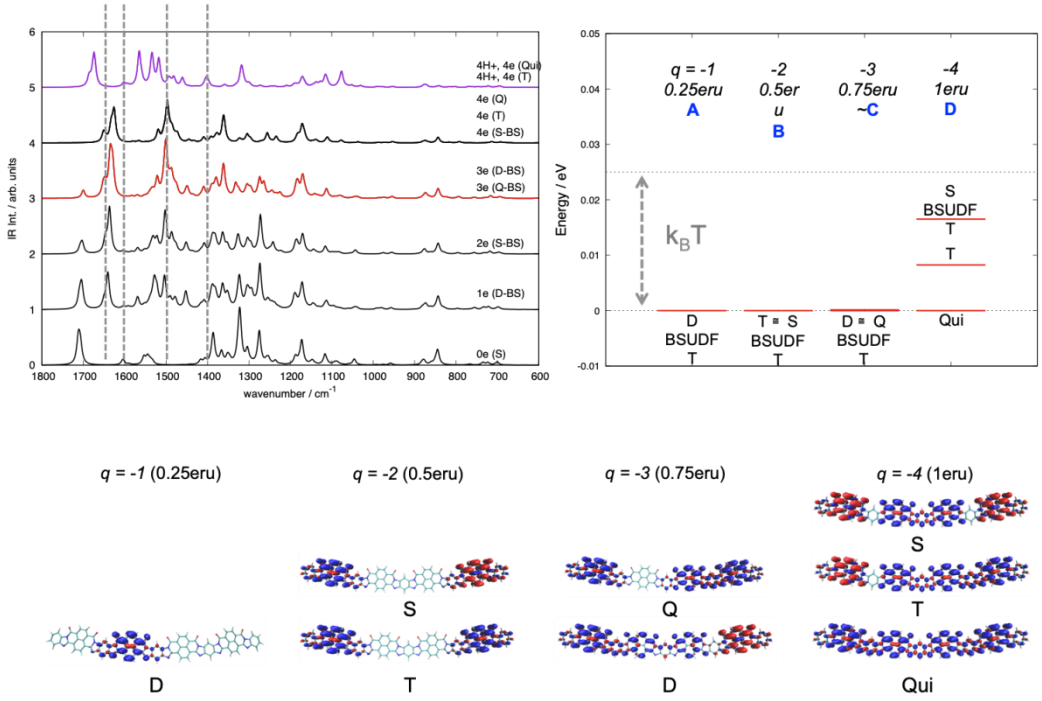


Figure S3

COMPARISON BETWEEN COMPUTED EXCITED STATES FOR *cis* AND *trans* CONFORMER (case of BBL4).

Here below are reported the computed (TDDFT, ωB97X-D/6-31G*) excitation energies for each species of BBL4, *cis* and *trans* conformers (most stable state is shown). BS indicates the use of a BS wavefunction on top of a BS optimized geometries.

BBL4 cis, P- (D) – TD-BS-UDFT

Excited State	1	1.1476 eV	1080.34 nm	f= 0.0055	<S**2>=0.850
Excited State	2	1.2288 eV	1008.97 nm	f= 0.0074	<S**2>=0.855
Excited State	3	1.2994 eV	954.20 nm	f= 0.0001	<S**2>=0.787
Excited State	4	1.5893 eV	780.13 nm	f= 0.0001	<S**2>=2.766
Excited State	5	1.5988 eV	775.50 nm	f= 0.0001	<S**2>=2.765
Excited State	6	1.6874 eV	734.77 nm	f= 0.0000	<S**2>=2.776
Excited State	7	1.9242 eV	644.35 nm	f= 0.0288	<S**2>=0.818
Excited State	8	2.1633 eV	573.13 nm	f= 0.4991	<S**2>=1.062
Excited State	9	2.4098 eV	514.50 nm	f= 0.1844	<S**2>=1.996
Excited State	10	2.4643 eV	503.12 nm	f= 0.1822	<S**2>=2.045
Excited State	**11**	**2.5176 eV**	**492.47 nm**	**f= 2.3441**	**<S**2>=1.363**
Excited State	12	2.6086 eV	475.29 nm	f= 0.1113	<S**2>=1.277
Excited State	13	2.6391 eV	469.80 nm	f= 0.0018	<S**2>=2.376
Excited State	14	2.6619 eV	465.77 nm	f= 0.0088	<S**2>=2.365
Excited State	15	2.7034 eV	458.63 nm	f= 0.2845	<S**2>=1.087
Excited State	16	2.7099 eV	457.52 nm	f= 0.2046	<S**2>=1.611
Excited State	17	2.8442 eV	435.92 nm	f= 0.0050	<S**2>=2.732
Excited State	18	2.8529 eV	434.59 nm	f= 0.4027	<S**2>=0.916
Excited State	19	2.8924 eV	428.65 nm	f= 0.1354	<S**2>=0.920
Excited State	20	2.9215 eV	424.38 nm	f= 0.1566	<S**2>=0.994
Excited State	21	2.9422 eV	421.40 nm	f= 0.0915	<S**2>=2.290
Excited State	22	2.9668 eV	417.90 nm	f= 0.0911	<S**2>=1.490
Excited State	23	2.9802 eV	416.03 nm	f= 0.0044	<S**2>=1.792
Excited State	24	3.0491 eV	406.63 nm	f= 0.0000	<S**2>=2.721
Excited State	25	3.0576 eV	405.50 nm	f= 0.0048	<S**2>=2.598

BBL4 cis, B- (S) – TD-BS-UDFT

Excited State	1	1.2779 eV	970.20 nm	f= 0.0091	<S**2>=1.134
Excited State	2	1.2781 eV	970.06 nm	f= 0.0033	<S**2>=1.133
Excited State	3	1.5925 eV	778.56 nm	f= 0.0001	<S**2>=3.043
Excited State	4	1.6210 eV	764.86 nm	f= 0.0001	<S**2>=3.042
Excited State	5	1.9724 eV	628.58 nm	f= 0.0130	<S**2>=1.091
Excited State	6	1.9731 eV	628.36 nm	f= 0.0773	<S**2>=1.091
Excited State	7	2.0845 eV	594.79 nm	f= 0.0002	<S**2>=1.063
Excited State	8	2.0846 eV	594.77 nm	f= 0.0018	<S**2>=1.063
Excited State	9	2.1717 eV	570.92 nm	f= 0.5858	<S**2>=1.276
Excited State	10	2.1770 eV	569.52 nm	f= 0.0120	<S**2>=1.276
Excited State	11	2.4866 eV	498.60 nm	f= 0.8740	<S**2>=1.961
Excited State	12	2.5034 eV	495.26 nm	f= 0.0071	<S**2>=2.383
Excited State	13	2.5827 eV	480.06 nm	f= 2.2723	<S**2>=1.885
Excited State	14	2.6489 eV	468.05 nm	f= 0.0209	<S**2>=1.521
Excited State	15	2.6655 eV	465.14 nm	f= 0.0005	<S**2>=2.820
Excited State	16	2.6933 eV	460.35 nm	f= 0.0006	<S**2>=2.481
Excited State	17	2.7032 eV	458.66 nm	f= 0.0927	<S**2>=1.367
Excited State	18	2.7067 eV	458.07 nm	f= 0.0029	<S**2>=1.485
Excited State	19	2.7367 eV	453.04 nm	f= 0.6569	<S**2>=1.354
Excited State	20	2.7417 eV	452.22 nm	f= 0.0136	<S**2>=1.554

BBL4 cis, q=3e- (D) – TD-BS-UDFT

Excited State	1	1.1842 eV	1046.95 nm	f= 0.0086	<S**2>=1.919
Excited State	2	1.5807 eV	784.38 nm	f= 0.0001	<S**2>=3.822
Excited State	3	1.8712 eV	662.59 nm	f= 0.0224	<S**2>=1.915
Excited State	4	1.9328 eV	641.47 nm	f= 0.0546	<S**2>=1.882
Excited State	5	1.9984 eV	620.43 nm	f= 0.0343	<S**2>=1.875
Excited State	6	2.0760 eV	597.22 nm	f= 0.0023	<S**2>=1.849
Excited State	7	2.0810 eV	595.79 nm	f= 0.0192	<S**2>=1.906
Excited State	8	2.1351 eV	580.70 nm	f= 0.9879	<S**2>=2.057
Excited State	9	2.1587 eV	574.34 nm	f= 0.0213	<S**2>=2.060
Excited State	10	2.1767 eV	569.59 nm	f= 0.1321	<S**2>=2.048
Excited State	11	2.4421 eV	507.70 nm	f= 0.3599	<S**2>=2.895
Excited State	12	2.5707 eV	482.30 nm	f= 2.2852	<S**2>=2.472
Excited State	13	2.6622 eV	465.71 nm	f= 0.1269	<S**2>=2.853
Excited State	14	2.6713 eV	464.13 nm	f= 0.1080	<S**2>=2.167
Excited State	15	2.6750 eV	463.48 nm	f= 0.0793	<S**2>=2.033
Excited State	16	2.6866 eV	461.50 nm	f= 0.0288	<S**2>=2.065
Excited State	17	2.6950 eV	460.06 nm	f= 0.2610	<S**2>=2.725
Excited State	18	2.7469 eV	451.36 nm	f= 0.3780	<S**2>=2.156
Excited State	19	2.7858 eV	445.06 nm	f= 0.0132	<S**2>=2.049
Excited State	20	2.8100 eV	441.22 nm	f= 0.0004	<S**2>=1.078
Excited State	21	2.8829 eV	430.06 nm	f= 0.0165	<S**2>=3.713
Excited State	22	2.9353 eV	422.39 nm	f= 0.0415	<S**2>=1.931
Excited State	23	2.9749 eV	416.77 nm	f= 0.0717	<S**2>=3.395
Excited State	24	2.9938 eV	414.14 nm	f= 0.0245	<S**2>=2.641
Excited State	25	3.0727 eV	403.50 nm	f= 0.1824	<S**2>=2.677
Excited State	26	3.1228 eV	397.03 nm	f= 0.0003	<S**2>=0.894
Excited State	27	3.1727 eV	390.78 nm	f= 0.0253	<S**2>=2.784
Excited State	28	3.2007 eV	387.37 nm	f= 0.1060	<S**2>=2.558
Excited State	29	3.2900 eV	376.85 nm	f= 0.0096	<S**2>=2.309
Excited State	30	3.3172 eV	373.77 nm	f= 0.0375	<S**2>=2.678

BBL4 cis, q=4e- (Qui) – TD-BS-UDFT

Excited State	1	1.9728 eV	628.48 nm	f= 0.0795	<S**2>=6.171
Excited State	2	1.9761 eV	627.43 nm	f= 0.0244	<S**2>=6.165
Excited State	3	1.9910 eV	622.71 nm	f= 0.0360	<S**2>=6.165
Excited State	4	1.9922 eV	622.34 nm	f= 0.0171	<S**2>=6.160
Excited State	5	2.1023 eV	589.75 nm	f= 1.6080	<S**2>=6.328
Excited State	6	2.1384 eV	579.79 nm	f= 0.0394	<S**2>=6.332
Excited State	7	2.1441 eV	578.27 nm	f= 0.0010	<S**2>=6.349
Excited State	8	2.1475 eV	577.33 nm	f= 0.0000	<S**2>=6.336
Excited State	9	2.6240 eV	472.50 nm	f= 2.3877	<S**2>=6.232
Excited State	10	2.6325 eV	470.98 nm	f= 0.5982	<S**2>=6.349
Excited State	11	2.6334 eV	470.81 nm	f= 0.0004	<S**2>=6.299
Excited State	12	2.6697 eV	464.42 nm	f= 0.0000	<S**2>=6.329
Excited State	13	2.6706 eV	464.26 nm	f= 0.0441	<S**2>=6.303
Excited State	14	2.7037 eV	458.57 nm	f= 0.0469	<S**2>=6.311
Excited State	15	2.7753 eV	446.73 nm	f= 0.0352	<S**2>=6.357
Excited State	16	2.8258 eV	438.76 nm	f= 0.0006	<S**2>=6.354
Excited State	17	2.9739 eV	416.90 nm	f= 0.0124	<S**2>=6.876
Excited State	18	2.9740 eV	416.89 nm	f= 0.0487	<S**2>=6.888
Excited State	19	3.0314 eV	409.00 nm	f= 0.0023	<S**2>=7.261
Excited State	20	3.0565 eV	405.65 nm	f= 0.2085	<S**2>=6.674
Excited State	21	3.0639 eV	404.66 nm	f= 0.0098	<S**2>=6.584
Excited State	22	3.1414 eV	394.68 nm	f= 0.6020	<S**2>=6.730
Excited State	23	3.2228 eV	384.71 nm	f= 0.0123	<S**2>=6.949
Excited State	24	3.2765 eV	378.41 nm	f= 0.0428	<S**2>=7.061
Excited State	25	3.3293 eV	372.41 nm	f= 0.0025	<S**2>=7.161
Excited State	26	3.3299 eV	372.34 nm	f= 0.0130	<S**2>=6.785
Excited State	27	3.3854 eV	366.23 nm	f= 0.0002	<S**2>=6.433
Excited State	28	3.4258 eV	361.91 nm	f= 0.0449	<S**2>=6.812
Excited State	29	3.5210 eV	352.13 nm	f= 0.0010	<S**2>=6.495
Excited State	30	3.5556 eV	348.71 nm	f= 0.0046	<S**2>=6.400

BBL4 trans, P- (D) – TD-BS-UDFT

```
Excited State   1      0.9720 eV 1275.60 nm  f= 0.5538  <S**2>=1.073
Excited State   2      1.1415 eV 1086.16 nm  f= 0.1101  <S**2>=1.208
Excited State   3      1.3918 eV  890.82 nm  f= 0.0022  <S**2>=0.946
Excited State   4      1.6345 eV  758.53 nm  f= 0.2407  <S**2>=2.423
Excited State   5      1.6903 eV  733.50 nm  f= 0.1389  <S**2>=2.353
Excited State   6      1.7339 eV  715.06 nm  f= 0.0289  <S**2>=2.612
Excited State   7      1.9736 eV  628.23 nm  f= 0.0261  <S**2>=0.842
Excited State   8      2.0999 eV  590.43 nm  f= 0.9297  <S**2>=1.120
Excited State   9      2.3182 eV  534.83 nm  f= 0.0031  <S**2>=2.555
Excited State  10      2.4074 eV  515.02 nm  f= 0.0238  <S**2>=2.499
Excited State  11      2.5254 eV  490.95 nm  f= 1.0964  <S**2>=0.969
Excited State  12      2.5776 eV  481.01 nm  f= 0.3449  <S**2>=2.309
Excited State  13      2.6102 eV  475.01 nm  f= 0.3450  <S**2>=1.213
Excited State  14      2.7157 eV  456.54 nm  f= 0.0043  <S**2>=1.368
Excited State  15      2.7803 eV  445.94 nm  f= 0.0012  <S**2>=2.117
Excited State  16      2.8088 eV  441.41 nm  f= 0.0008  <S**2>=1.670
Excited State  17      2.8492 eV  435.15 nm  f= 0.0025  <S**2>=2.281
Excited State  18      2.9079 eV  426.37 nm  f= 0.0458  <S**2>=1.230
Excited State  19      2.9542 eV  419.69 nm  f= 0.9844  <S**2>=0.824
Excited State  20      3.0308 eV  409.08 nm  f= 0.0001  <S**2>=2.553
```

BBL4 trans, B- (D) – TD-BS-UDFT

```
Excited State   1      1.0841 eV 1143.61 nm  f= 0.6503  <S**2>=1.441
Excited State   2      1.1021 eV 1124.97 nm  f= 0.0000  <S**2>=1.503
Excited State   3      1.6625 eV  745.79 nm  f= 0.0000  <S**2>=2.622
Excited State   4      1.7015 eV  728.67 nm  f= 0.4193  <S**2>=2.614
Excited State   5      1.9622 eV  631.88 nm  f= 0.0890  <S**2>=1.095
Excited State   6      1.9625 eV  631.77 nm  f= 0.0000  <S**2>=1.098
Excited State   7      2.1123 eV  586.97 nm  f= 0.0000  <S**2>=1.413
Excited State   8      2.1432 eV  578.49 nm  f= 0.0047  <S**2>=1.089
Excited State   9      2.1508 eV  576.44 nm  f= 1.0746  <S**2>=1.266
Excited State  10      2.1596 eV  574.10 nm  f= 0.0000  <S**2>=1.226
Excited State  11      2.3033 eV  538.30 nm  f= 0.0000  <S**2>=2.488
Excited State  12      2.4518 eV  505.68 nm  f= 0.1233  <S**2>=2.594
Excited State  13      2.5618 eV  483.98 nm  f= 2.2617  <S**2>=1.298
Excited State  14      2.6228 eV  472.72 nm  f= 0.0000  <S**2>=1.184
Excited State  15      2.6834 eV  462.04 nm  f= 0.0000  <S**2>=1.433
Excited State  16      2.6928 eV  460.43 nm  f= 0.0402  <S**2>=1.454
Excited State  17      2.7894 eV  444.48 nm  f= 0.2113  <S**2>=1.275
Excited State  18      2.7953 eV  443.54 nm  f= 0.0000  <S**2>=1.388
Excited State  19      2.8585 eV  433.73 nm  f= 0.0000  <S**2>=2.755
Excited State  20      2.8655 eV  432.68 nm  f= 0.0088  <S**2>=2.817
Excited State  21      2.9529 eV  419.88 nm  f= 0.0000  <S**2>=2.245
Excited State  22      3.0105 eV  411.84 nm  f= 0.0449  <S**2>=1.778
Excited State  23      3.0500 eV  406.50 nm  f= 0.0000  <S**2>=2.303
Excited State  24      3.0899 eV  401.26 nm  f= 0.2667  <S**2>=1.224
Excited State  25      3.1394 eV  394.93 nm  f= 0.0000  <S**2>=1.405
Excited State  26      3.1774 eV  390.20 nm  f= 0.1572  <S**2>=1.364
Excited State  27      3.2263 eV  384.29 nm  f= 0.0000  <S**2>=1.292
Excited State  28      3.2793 eV  378.08 nm  f= 0.3047  <S**2>=1.704
Excited State  29      3.3369 eV  371.55 nm  f= 0.0000  <S**2>=2.878
Excited State  30      3.3449 eV  370.66 nm  f= 0.0735  <S**2>=2.412
```

BBL4 trans, 3e- (D) – TD-BS-UDFT

```
Excited State   1      0.9938 eV 1247.56 nm  f= 0.4514  <S**2>=4.187
Excited State   2      1.5820 eV  783.70 nm  f= 0.0320  <S**2>=5.136
Excited State   3      1.8226 eV  680.26 nm  f= 0.8475  <S**2>=4.272
Excited State   4      1.8988 eV  652.95 nm  f= 0.0603  <S**2>=3.904
Excited State   5      1.9525 eV  634.99 nm  f= 0.0013  <S**2>=3.870
Excited State   6      2.0173 eV  614.60 nm  f= 0.5856  <S**2>=4.040
Excited State   7      2.0463 eV  605.88 nm  f= 0.1894  <S**2>=4.101
Excited State   8      2.1112 eV  587.26 nm  f= 0.0174  <S**2>=3.947
Excited State   9      2.1767 eV  569.61 nm  f= 0.4225  <S**2>=4.017
Excited State  10      2.2236 eV  557.58 nm  f= 0.0010  <S**2>=3.992
Excited State  11      2.3529 eV  526.95 nm  f= 0.0208  <S**2>=5.050
```

Excited State	12	2.5565 eV	484.98 nm	f= 1.4410	<S**2>=4.128
Excited State	13	2.5904 eV	478.63 nm	f= 0.5607	<S**2>=4.163
Excited State	14	2.6460 eV	468.57 nm	f= 0.0309	<S**2>=4.095
Excited State	15	2.6686 eV	464.60 nm	f= 0.0135	<S**2>=4.149
Excited State	16	2.7046 eV	458.41 nm	f= 0.0666	<S**2>=3.967
Excited State	17	2.7738 eV	446.98 nm	f= 0.7374	<S**2>=4.015
Excited State	18	2.8032 eV	442.29 nm	f= 0.0034	<S**2>=4.179
Excited State	19	2.8571 eV	433.95 nm	f= 0.0185	<S**2>=4.508
Excited State	20	2.8972 eV	427.95 nm	f= 0.0026	<S**2>=5.031
Excited State	21	2.9343 eV	422.53 nm	f= 0.0029	<S**2>=4.914
Excited State	22	3.0178 eV	410.84 nm	f= 0.0154	<S**2>=4.527
Excited State	23	3.0733 eV	403.42 nm	f= 0.0401	<S**2>=4.277
Excited State	24	3.1178 eV	397.67 nm	f= 0.0667	<S**2>=4.108
Excited State	25	3.1298 eV	396.14 nm	f= 0.0032	<S**2>=5.039
Excited State	26	3.2002 eV	387.43 nm	f= 0.0045	<S**2>=4.728
Excited State	27	3.2110 eV	386.13 nm	f= 0.0186	<S**2>=4.973
Excited State	28	3.2929 eV	376.52 nm	f= 0.0296	<S**2>=4.490
Excited State	29	3.3617 eV	368.81 nm	f= 0.0059	<S**2>=4.675
Excited State	30	3.4124 eV	363.34 nm	f= 0.0196	<S**2>=4.316

BBL4 trans, 4e- (S) – TD-BS-UDFT

Excited State	1	1.7090 eV	725.49 nm	f= 1.5923	<S**2>=1.805
Excited State	2	1.7520 eV	707.69 nm	f= 0.0000	<S**2>=1.762
Excited State	3	1.9240 eV	644.40 nm	f= 0.3149	<S**2>=2.131
Excited State	4	1.9326 eV	641.53 nm	f= 0.0000	<S**2>=2.153
Excited State	5	1.9975 eV	620.70 nm	f= 0.0000	<S**2>=2.044
Excited State	6	2.0080 eV	617.45 nm	f= 0.0117	<S**2>=2.026
Excited State	7	2.0881 eV	593.76 nm	f= 0.0000	<S**2>=2.129
Excited State	8	2.0973 eV	591.17 nm	f= 1.1994	<S**2>=2.199
Excited State	9	2.3385 eV	530.18 nm	f= 0.0739	<S**2>=1.944
Excited State	10	2.3440 eV	528.94 nm	f= 0.0000	<S**2>=1.908
Excited State	11	2.4937 eV	497.19 nm	f= 0.0000	<S**2>=2.388
Excited State	12	2.5727 eV	481.93 nm	f= 0.6514	<S**2>=1.900
Excited State	13	2.6127 eV	474.55 nm	f= 0.3877	<S**2>=2.399
Excited State	14	2.6431 eV	469.08 nm	f= 0.0000	<S**2>=2.363
Excited State	15	2.6478 eV	468.25 nm	f= 0.0332	<S**2>=2.326
Excited State	16	2.6970 eV	459.72 nm	f= 0.0000	<S**2>=2.150
Excited State	17	2.7227 eV	455.37 nm	f= 1.3577	<S**2>=2.157
Excited State	18	2.7669 eV	448.09 nm	f= 0.0000	<S**2>=2.238
Excited State	19	2.8549 eV	434.28 nm	f= 0.0173	<S**2>=2.552
Excited State	20	2.8731 eV	431.53 nm	f= 0.0000	<S**2>=2.400
Excited State	21	2.9295 eV	423.23 nm	f= 0.0000	<S**2>=2.416
Excited State	22	2.9708 eV	417.34 nm	f= 0.0590	<S**2>=2.172
Excited State	23	3.0536 eV	406.03 nm	f= 0.0000	<S**2>=2.312
Excited State	24	3.1121 eV	398.39 nm	f= 0.0823	<S**2>=2.303
Excited State	25	3.2614 eV	380.15 nm	f= 0.0000	<S**2>=2.712
Excited State	26	3.3112 eV	374.44 nm	f= 0.0269	<S**2>=2.490
Excited State	27	3.3423 eV	370.95 nm	f= 0.0000	<S**2>=2.570
Excited State	28	3.3878 eV	365.97 nm	f= 0.0000	<S**2>=2.876
Excited State	29	3.3934 eV	365.37 nm	f= 0.0065	<S**2>=2.607
Excited State	30	3.4680 eV	357.51 nm	f= 0.0116	<S**2>=2.762

IR ASSIGNMENT FOR THE PROTONATED SPECIES

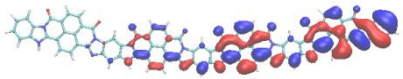
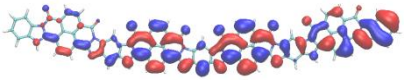
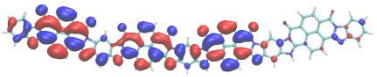
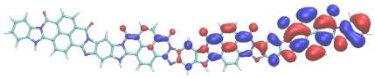
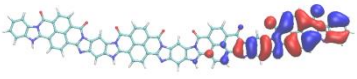
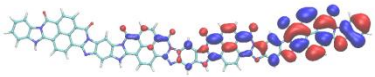
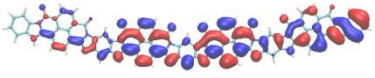
Most intense IR active band as computed (□B97X-D/6-31G*) for BBL4 *cis* 4H+ (Quintet state).

ν theo. cm^{-1}	Assignment
1692, 1698, 1700, 1704, 1729, 1729, 1747, 1752	8x CO str.
990	CH rocking coupled with NH rocking localised on one benzophenantroline

MOS FOR THE PROTONATED BBL4 4H+ SPECIES.

Molecular orbitals (beta) involved in the low-energy electronic transition (S1), as computed at the TD-DFT level (UωB97X-D/6-31G*, Quintet state) for BBL4 *cis* 4H+ (see Figure 6 of the manuscript).

S_1: E = 1.12 eV, f = 0.0517

Occ.	Virt.	Coeff.
 SOMO□-2	 SUMO□+1	0.67
 SOMO□-2	 SUMO□+2	-0.47
 SOMO□-2	 SUMO□+3	0.10
 SOMO□-2	 SUMO□+5	-0.28
 SOMO□	 SUMO□+1	-0.35
 SOMO□-2	 SUMO□+2	0.23