Electronic Supplementary information for:

Time-resolved photoelectron imaging of the chloranil radical anion: Ultrafast relaxation of electronically excited electron acceptor states

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In order to establish the electronic similarities between the chloranil radical anion ($CA^{\bullet-}$) and the *para*-benzoquinone radical anion ($pBQ^{\bullet-}$) we have performed DFT and TD-DFT calculations with the B3LYP functional and cc-pVTZ basis set, using the Gaussian09 software package.[1] $CA^{\bullet-}$ and $pBQ^{\bullet-}$, as well as their neutral ground states, are planar and have D_{2h} symmetry. Table S1 shows the relevant molecular orbitals (MOs) and their symmetry labels (details of axes are given in the paper, Fig. 2). The list of MOs and their occupation is shown for the HOMO–3 to the LUMO+2 (where HOMO and LUMO are the highest occupied and lowest unoccupied molecular orbital of the corresponding neutral, respectively).

***p*-Benzoquinone**		**Chloranil**
a_g		a_g
a_u		a_u
b_{2g}	↑	b_{2g}
b_{3g}	↑↓	b_{1g}
b_{2u}	↑↓	b_{3g}
b_{1g}	↑↓	b_{2u}
b_{3u}	↑↓	b_{3u}

Table S1: Calculated frontier molecular orbitals for the radical anions of *p*BQ and CA. Also indicated are the orbital occupancies. In $CA^{\bullet-}$ the b_{1g} MO is destabilised with respect to the same orbital in $pBQ^{\bullet-}$ and places it above the b_{3g} in energy. All other molecular orbitals are identical.

The MOs are identical, apart from the orbital of b_{1g} symmetry in $CA^{\bullet-}$, which is destabilised in comparison to $pBQ^{\bullet-}$ and shifts in energy above the b_{2u} and b_{3g} MOs. This can be rationalised by comparing the MO iso-surfaces, which are shown in Fig. S1. The repulsive interaction along the C–Cl bonds, which is absent in $pBQ^{\bullet-}$ and is much less pronounced for the b_{2u} and b_{3g} MOs, leads to a higher electronic energy for the b_{1g} MO. Apart from this MO, the electronic structure between the two systems is identical, in terms of symmetries, MO shapes and relative MO ordering. However, the b_{1g}, b_{3g} and b_{2u} orbitals all lie very close in energy and small effects can alter the order. Indeed, using a higher-level of theory, Honda *et al*. have shown that the b_{1g} is also the HOMO of *p*BQ, in contradiction to the b_{3g} MO predicted using our (lower) level of theory.[2] As the b_{1g} is destabilised further in CA relative to *p*BQ, it is expected that the HOMO of both *p*BQ and CA is the b_{1g} and this is supported by other theoretical studies.[3] Moreover, the HOMO is not involved in the excited states discussed in the manuscript and hence the identity of the HOMO has no consequences to our interpretations.

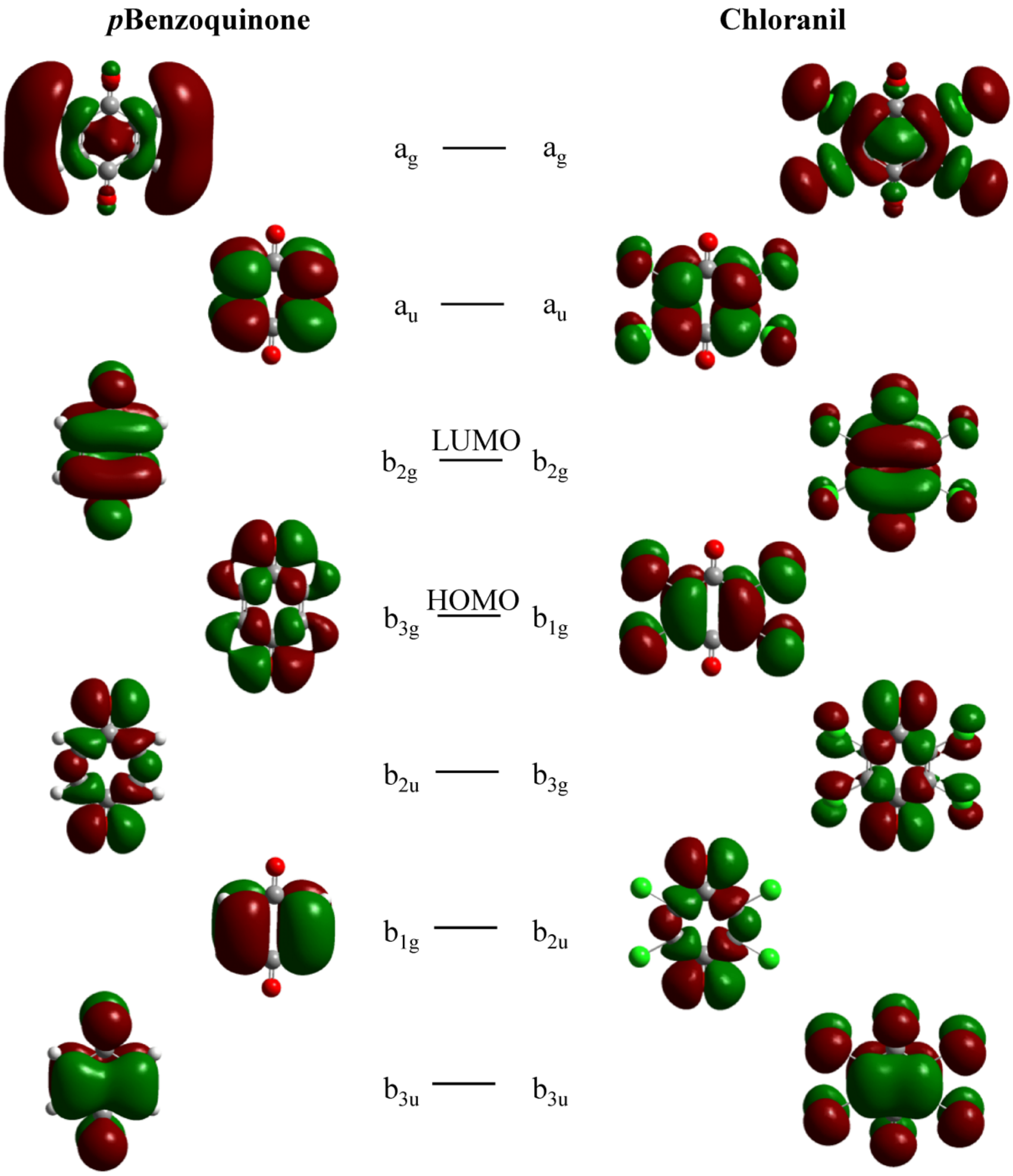

Fig. S1: Molecular orbital iso-surfaces for frontier orbitals of the radical anions of *p*BQ and CA. The repulsive interaction along the C–Cl bond in the b_{1g} destabilises this orbital in CA relative to *p*BQ.

In order to determine the relative importance of electronic transitions, in particular the relative ordering of the ^2A_u and $^2B_{3u}$, and the presence of low-lying nπ* states, the first 7 electronically excited states have been calculated for $CA^{\bullet-}$ and *p*$BQ^{\bullet-}$. The transition ordering, state term symbols and major contribution to these transitions have been summarised in Table S2. As expected, the similarities between the two are striking. The only difference in ordering of the excited states is due to the higher energy of the $^2b_{1g}$ MO in $CA^{\bullet-}$, and we note that the two main transitions of interest in the current work do not involve this MO.

The first two excited states in $CA^{\bullet-}$ and *p*$BQ^{\bullet-}$ are the $^2B_{3g}$ and $^2B_{2u}$ state and clearly correspond to nπ* states. For *p*$BQ^{\bullet-}$, this leads to the low energy tail observed in the absorption spectrum and, given that in $CA^{\bullet-}$ the same states are present and the absorption spectrum exhibits a similar low-energy tail, it is reasonable to assign this tail to nπ* states for $CA^{\bullet-}$.[4]

The two bright states in the absorption spectrum around 500 nm correspond to the ^2A_u and the $^2B_{3u}$. Both are ππ* transitions but the $^2B_{3u}$ involves excitation from the core b_{3u} orbital to the b_{2g}, whereas the ^2A_u involves excitation from the lone electron in the b_{2g} MO to the LUMO + 1, which is an a_u MO. Electron loss from the latter will lead to the neutral CA in its ground state configuration (i.e. all MOs fully occupied up to the LUMO), while for the $^2B_{3u}$ state, the electronic configuration is such that there is one electron in the b_{3u} and two electrons in the b_{2g}. Electron loss from the b_{2g} orbital will therefore lead to an electronically excited state of the neutral.

The key conclusion from our calculations is that indeed $CA^{\bullet-}$ and *p*$BQ^{\bullet-}$ are electronically very similar and hence, we can have some confidence in interpreting the spectroscopy of the electronic structure of $CA^{\bullet-}$ using the much more studied *p*$BQ^{\bullet-}$ as a template.

#	**p-Benzoquinone**	**Chloranil**
1	$^2B_{3g} : b_{3g} \rightarrow b_{2g}$	$^2B_{3g} : b_{3g} \rightarrow b_{2g}$
2	$^2B_{2u} : b_{2u} \rightarrow b_{2g}$	$^2B_{2u} : b_{2u} \rightarrow b_{2g}$
3	$\mathbf{^2A_u : b_{2g} \rightarrow a_u}$	$^2B_{1g} : b_{1g} \rightarrow b_{2g}$
4	$^2B_{1g} : b_{1g} \rightarrow b_{2g}$	$\mathbf{^2A_u : b_{2g} \rightarrow a_u}$
5	$\mathbf{^2B_{3u} : b_{3u} \rightarrow b_{2g}}$	$\mathbf{^2B_{3u} : b_{3u} \rightarrow b_{2g}}$
6	$^2B_{1g} : b_{1g} \rightarrow a_u$	$^2A_g : b_{2g} \rightarrow a_g$
7	$^2A_g : b_{2g} \rightarrow a_g$	$^2B_{1g} : b_{1g} \rightarrow a_u$

Table S2: First 7 excited states calculated for *p*$BQ^{\bullet-}$ and $CA^{\bullet-}$. The two bright states that are accessible around 500 nm are indicated in bold.

References

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