Radiation damage in biomimetic dye molecules for solar cells

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A significant obstacle to organic photovoltaics is radiation damage, either directly by photochemical reactions or indirectly via hot electrons. Such effects are investigated for biomimetic dye molecules for solar cells (phthalocyanines) and for a biological analog (the charge transfer protein cytochrome c). Both feature a central transition metal atom (or H_2) surrounded by nitrogen atoms. Soft x-ray absorption spectroscopy and photoelectron spectroscopy are used to identify three types of radiation-induced changes in the electronic structure of these molecules. (1) The peptide bonds along the backbone of the protein are readily broken, while the nitrogen cage remains rather stable in phthalocyanines. This finding suggests minimizing peptide attachments to biologically inspired molecules for photovoltaic applications. (2) The metal atom in the protein changes its 3d electron configuration under irradiation. (3) The Fermi level E_F shifts relative to the band gap in phthalocyanine films due to radiation-induced gap states. This effect has little influence on the optical absorption, but it changes the lineup between the energy levels of the absorbing dye and the acceptor/donor electrodes that collect the charge carriers in a solar cell. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Tailored organic dye molecules provide versatile and inexpensive materials for light emitting diodes[1] as well as for dye-sensitized solar cells.[2–8] However, the lifetime and efficiency of molecular electronic devices are limited by hot electron damage. In organic light emitting diodes (OLEDs), for example, the combination of hot electrons and an oxidant initially posed a serious lifetime problem.[1,9] That was eventually solved by carefully sealing out oxidizing contaminants, such as water. Hot electrons originate not only from charge injection in OLEDs, they are also created by absorbed light in solar cells. Therefore, one might expect similar lifetime problems to reappear in photovoltaics.

Biomolecules have been invoked as models for designing and optimizing organic molecules for photovoltaics.[10] They are particularly efficient at separating the initial electron-hole pair. However, part of the photosynthetic center in plants actually self-destructs after about an hour of operation and needs to be newly synthesized by the plant (Ref. 10, p. 146). Biological systems, such as photosystem II, are highly sensitive to radiation damage.[11] In order to understand the processes that can destroy molecular photovoltaic devices it is useful to investigate potential mechanisms of radiation damage in both biomolecules and their analogs in photovoltaics, such as porphyrins and phthalocyanines.[3,12] Particularly important are the electronic changes induced by radiation.

In a recent publication[12] we investigated the electronic structure of unoccupied molecular orbitals in biomimetic dye molecules for solar cells.[3–8] A class of molecules was chosen where the active center consists of a transition metal atom surrounded by a cage of nitrogen atoms, i.e., porphyrins, phthalocyanines, and the charge transfer protein cytochrome c. Near edge x-ray absorption fine structure spectroscopy (NEXAFS) was used to reveal the oxidation state of the transition metal atom and to find the unoccupied orbitals of the nitrogen cage.

Here we apply similar techniques to go one step further and pinpoint how radiation affects the electronic structure of these molecules. The changes in the unoccupied molecular orbitals are investigated on an atom-specific basis via NEXAFS, and those in the occupied orbitals by photoelectron spectroscopy.

Although radiation damage is initiated by soft x-ray photons in this work, the Auger decay of the core hole starts a cascade of secondary electron-hole pairs. These eventually accumulate within a few eV above the lowest unoccupied molecular orbital (LUMO), the analog of the conduction band minimum in semiconductors. The energy distribution of these secondary electrons begins to resemble that of the hot electrons injected into OLEDs or produced by UV photons in photovoltaics. Such hot electron damage presents a fundamental challenge to organic photovoltaics, as well as to molecular electronics in general. Despite these similarities one should not forget that the fragmentation of thin molecular films by soft x rays is a complex, multistep phenomenon that is difficult to model.[13–15]

Radiation is found to affect the electronic structure of dye molecules in several ways. (1) In biological dye molecules, such as the metalloprotein cytochrome c, radiation easily damages the peptide bond between the amino acids in the backbone of the protein. This finding suggests minimizing peptide attachments to biologically inspired molecules

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for photovoltaic applications. (2) The 3d electron configuration of the transition metal center changes under irradiation. This suggests considering the possibilities for healing this type of damage by converting the 3d electron configuration back to the ground state. (3) The Fermi level E_F shifts due to creation of defect states in the band gap of the dye molecule. This affects the level offset with the collector electrodes in a solar cell and thereby changes the carrier collection efficiency.[16]

II. EXPERIMENTAL METHODS

Empty molecular orbitals were probed by NEXAFS while occupied states were measured by photoelectron spectroscopy. Both types of measurements were performed with tunable synchrotron radiation from the Synchrotron Radiation Center (SRC) at the University of Wisconsin-Madison and from the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The experimental details (including sample preparation) are described in detail elsewhere.[12]

In NEXAFS, the incident soft x rays create core holes, which decay mainly into Auger electrons with kinetic energies of several hundreds of eV (≈700 eV for the Fe 2p core level, ≈400 eV for the N 1s core level). The energetic soft x-ray photons and Auger electrons are easily able to break bonds and to create new chemical species. Eventually, most of the Auger electrons decay via a cascade of electron-hole pair production processes and create an avalanche of secondary electrons (of the order 10^2 secondary electrons per incident photon in our case). Smaller energy losses to phonons create a further trickle down at the bottom of the secondary electron cascade and lead to an accumulation of electrons above the conduction band minimum, i.e., the LUMO of a molecular solid. Their spectrum resembles that of hot electrons in a solar cell. The energy of most secondary electrons is not enough to break bonds, but they are able to create defect states in the band gap of a molecular solid.

Most of the NEXAFS spectra shown here are taken by collecting all the electrons in the total electron yield mode. Fluorescence yield spectra were acquired simultaneously for the Fe 2p edge, which showed similar behavior. To monitor the flux of incident x rays we measured the current from a gold mesh in the beam line. To convert the current into a flux we assumed that the quantum yield of gold is 10% at ≈400 eV.[17,18]

For photoelectron spectroscopy a Scienta 200 photoelectron spectrometer was used in conjunction with *in situ* thin film sample preparation capabilities. Various photon energies from 34 to 90 eV were used to gather information about the orbital character via changes in the cross section of the transition metal 3d and the N 2s, 2p orbitals. The photon flux was kept very low by narrow slit settings of the monochromator, and the sensitivity of the electron spectrometer was increased by opening its slits and increasing the pass energy to 20 eV. Furthermore, the spectra are integrated over the acceptance angle of the spectrometer (≈12°).

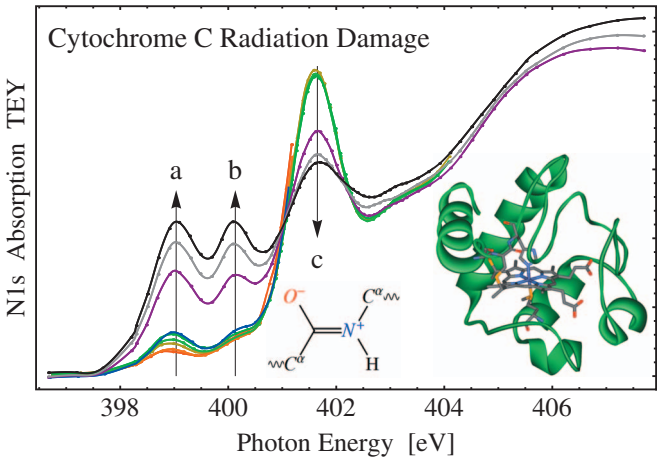

FIG. 1. Effect of radiation damage on cytochrome c, irradiated with photons at the N 1s edge (≈400 eV). The π^* orbital of the peptide bond at 401.7 eV is quenched and two π^* peaks are created at 399.1 and 400.2 eV by the product of the photochemical reaction. Such radiation-induced bond breaking in the backbone of cytochrome c suggests replacing complex protein structures by simpler molecules containing only the active heme region when designing biomimetic solar cells. The inset shows the structure of cytochrome c with the heme group inside (containing an Fe atom in a N cage).

III. BREAKUP OF THE PROTEIN BACKBONE, OBSERVED AT THE N 1s EDGE

The effect of radiation on the N 1s NEXAFS spectrum of cytochrome c is shown in Figs. 1 and 2. Pristine cytochrome c shows a dominant peak at 401.7 eV induced by transitions from the N 1s core level to the π^* orbitals of the 103 peptide bonds that connect the 104 amino acids in the backbone of this protein (peak c). The peptide bond is the double bond formed between two amino acids in peptides and proteins, connecting the amine nitrogen to the carbon in the carboxylic acid (inset in Fig. 1). After adding the covalent configuration to the (zwitter)-ionic configuration shown in Fig. 1, the bond orbital extends all the way to the oxygen

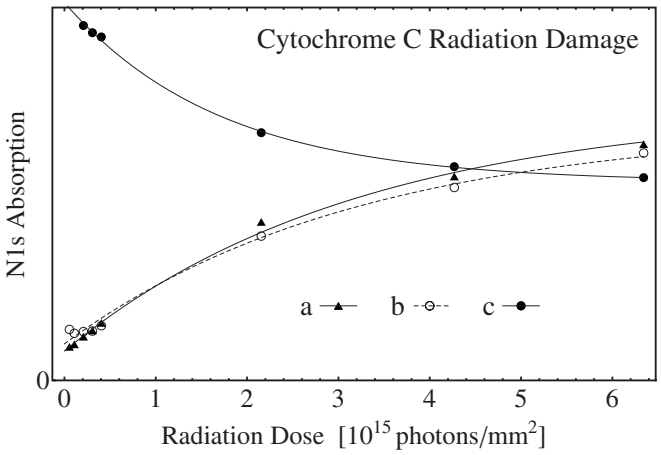

FIG. 2. The radiation-induced changes for the three nitrogen π^* orbitals observed in Fig. 1 (a=399.1 eV, b=400.2 eV, and c=401.7 eV). The peptide bond orbital (c) decays exponentially with increasing radiation dose, while the two radiation-induced π^* orbitals (a and b) grow at the same rate as c vanishes. The constant a/b intensity ratio is consistent with two nitrogen π^* orbitals at the site of the broken peptide bond.

atom. A more detailed discussion of the peptide bond and its orbital character is given in Refs. 12, 19, and 20.

During irradiation by ≈400 eV photons (during repeated scanning of NEXAFS spectra) the π^* orbital of the peptide bond rapidly decreases in intensity. At the same time two peaks at 399.1 and 400.2 eV grow in intensity (peaks a, b). All three peaks correspond to π^* orbitals at nitrogen sites. The exact identity of peaks a, b is still under investigation.[20] Similar radiation-induced peaks have been observed in bacterial surface proteins[21] as well as in phenylalanine and tyrosine.[22] In the first case an attack on the C=O group in the peptide bond was discussed, while in the second case partial dehydrogenation of the amino group was invoked. Nevertheless, we can clearly state from the disappearance of peak c that the peptide bond is broken, i.e., the backbone of the protein is attacked by exposure to radiation.

It would be interesting to know the radiation sensitivity of the remaining N atoms in cytochrome c, which form the cage around the Fe atom in the heme group (see the inset in Fig. 1). However, their NEXAFS signal is overwhelmed by the more numerous peptide bond orbitals (5 nitrogen atoms in the cage of the heme versus 103 nitrogen atoms in the peptide bonds of the backbone). The π^* orbitals of the nitrogen cage are expected in the same energy region as the damage peaks a and b, judging from the N 1s spectra of porphyrins and phthalocyanines (see Fig. 6 in Ref. 12). That makes the signal from the nitrogen cage even more difficult to discern. We have investigated the sensitivity of the analogous π^* orbitals of phthalocyanines to radiation damage and find them orders of magnitude less sensitive than the π^* orbital of the peptide bond.

Figure 2 quantifies the radiation-induced intensity changes of the π^* orbitals associated with the peptide bond (c) and its fragments (a, b). While peak c decays exponentially, peaks a and b grow exponentially at the same rate. That indicates a direct conversion of the peptide bond into a π bond at the same N site. There is a small residual height of peaks a and b at zero radiation exposure, which could either be due to residual radiation damage during the first scan or due to the nitrogen atoms in the heme group of cytochrome c.

Since the protein backbone is so sensitive to radiation it becomes clear that one should not go too far in imitating nature for the design of biomimetic solar cells. Instead, peptide attachments should be avoided and only the electronic structure of the photochemically active heme group should be replicated.

IV. CONFIGURATION CHANGE OF THE METAL ELECTRONS, OBSERVED AT THE Fe 2p EDGE

Irradiation does not only break the backbone of the protein in cytochrome c, but it also changes the electronic structure of the Fe atom in the heme group. Radiation effects show up clearly at the Fe 2p edge of the central metal atom, as shown in Fig. 3.

The interpretation of the Fe 2p edge requires a switch from single-electron molecular orbitals to a many-electron picture. The localized nature of the 2p-to-3d transitions enhances the Coulomb/exchange coupling among the valence

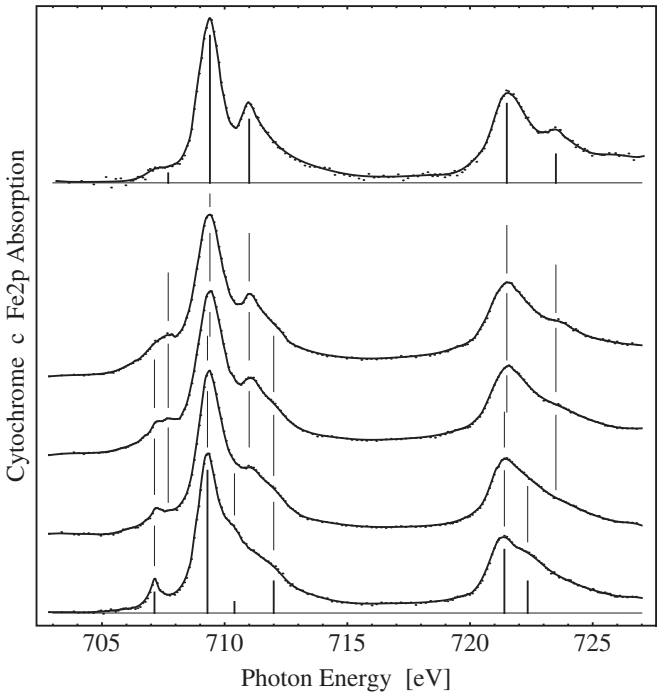

FIG. 3. Effect of irradiation on the Fe 2p edge of the central Fe atom in the heme group of cytochrome c. The bottom spectrum is for pristine cytochrome c, and the radiation dose increases toward the top spectrum. The change in the multiplet structure points to a change in the 3d spin configuration or in the crystal field at the Fe atom. It is too small to be caused by a change of the oxidation state.

electrons in the 3d shell and their interaction with the 2p core hole. The resulting NEXAFS spectrum exhibits a multiplet structure that needs to be considered as a whole instead of assigning peaks to individual orbitals. We use the multiplet pattern as a fingerprint of the oxidation state of the Fe atom. A full analysis would require theoretical modeling that combines the screened Coulomb/exchange interactions of the 3d electrons with each other and with the 2p core hole, as well as the ligand field interaction between the Fe 3d electrons and the crystal field created by the surrounding cage atoms.

The Fe 2p edge of cytochrome c in Fig. 3 exhibits a multiplet containing some surprisingly sharp features. They indicate that the Fe atom is disturbed rather weakly by the surrounding protein. The dominant peak at 709.3 eV shows little change with irradiation, i.e., an upwards shift by only 0.1 eV from bottom to top in Fig. 3. However, weaker features on either side of this peak vanish with irradiation, i.e., a sharp peak at 707.1 eV, a broad shoulder at 712.0 eV, and a weak shoulder at 710.4 eV. As their intensity decreases, two new features appear at 707.7 and 711.0 eV. Likewise, the main in the spin-orbit partner peak at 721.4 eV shifts up by only 0.1 eV with irradiation. A shoulder at 722.4 eV gives way to a peak at 723.5 eV in the fully irradiated spectrum at the top of Fig. 3.

The change in the multiplet structure indicates a change in the 3d electron configuration, which could be due to a different oxidation state, a different spin state, or a different crystal field at the Fe atom. Without a proper multiplet calculation[23,24] it is difficult to make quantitative statements. High spin would be favored in an isolated atom by Hund's

first rule, low spin comes into play for a molecule via covalent bonding to neighbor atoms by spin-paired electrons. However, one can draw one qualitative conclusion from the small shift of 0.1 eV observed for the main peak in the multiplet. With a change in the oxidation state one would expect a shift of the order 1 eV. For example, the oxidation of ferrocene to ferrocenium in a self-assembled monolayer causes the main peak in the Fe 2p edge to shift up by 0.8 eV.[25] Likewise, the oxidation of Fe^{2+}-phthalocyanine to Fe^{3+}Cl-phthalocyanine shifts the main Fe 2p absorption peak up by 2 eV.[12] Applying this qualitative criterion to cytochrome c indicates that the oxidation state of cytochrome c changes very little by irradiation. This observation points toward a change in the spin state or in the crystal field at the Fe site, or both. A level splitting induced by the crystal field can change the spin configuration. A less likely explanation for the small shift would be an incomplete conversion of the sample by irradiation. The top spectrum in Fig. 3 reflects the fully saturated spectral changes after prolonged irradiation.

The absolute oxidation state of cytochrome c can be inferred from the energy position of the main Fe 2p multiplet peak (709.3 eV in pristine cytochrome c). The best match occurs with Fe^{3+}Cl-octaethylporphyrin (709.2 eV), a decent match with Fe^{3+}Cl-phthalocyanine (708.8 eV), and a poor match with Fe^{2+}-phthalocyanine (706.8 eV).[12] This is consistent with a previous determination of the oxidation state from the Fe 1s absorption edge.[26] At a more detailed level one can compare the multiplet pattern with reference compounds. The Fe 2p multiplet structure has been investigated systematically in iron complexes from Fe^0 to Fe^{4+} in a study of x-ray photochemistry in iron complexes.[27] There is no obvious match with any of these reference compounds, though. Their local bonding around the Fe differs too much from that of cytochrome c. Some similarity appears when comparing cytochrome c to a set of reference compounds where Fe is surrounded by a three-dimensional cage of six nitrogen ligands.[24] The difficulty of finding a perfect match between multiplets is due to the sensitivity of the detailed multiplet pattern to the crystal field. This can be seen empirically by comparing the Fe 2p multiplet of cytochrome c with the multiplets for Fe^{3+}Cl-octaethylporphyrin, Fe^{3+}Cl-phthalocyanine, and Fe^{2+}-phthalocyanine (see Ref. 12). The multiplet of pristine cytochrome c does not match any of the other patterns. The likely reason is the three-dimensional character of the nitrogen cage in cytochrome c, which differs qualitatively from the two-dimensional nitrogen cages in phthalocyanines and porphyrins.

Both the change in the electron configuration at the Fe 2p edge and the breakup of the peptide bond at the N 1s edge happen at very low radiation dose. Narrow monochromator slits and additional attenuation of the synchrotron light by a filter are required to keep cytochrome c in the pristine state. The Fe phthalocyanines and porphyrins are orders of magnitude less sensitive to irradiation. Clearly, we can make a strong case against keeping peptide attachments in biomimetic dye molecules for applications in solar cells. The electronic structure of the heme group has to be reproduced by other types of chemical modifications.

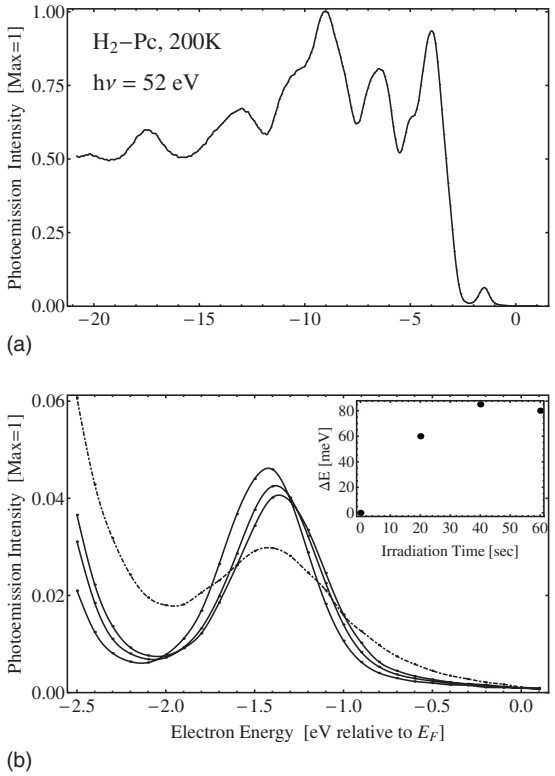

FIG. 4. Radiation-induced shift of the HOMO relative to the Fermi level E_F for H_2-phthalocyanine. The top panel gives an overview spectrum of the occupied orbitals. The bottom panel zooms in on the HOMO and shows its upwards shift with irradiation. Spectra are shown for 0, 20, and 40 s exposure (full lines) and for a much higher exposure (dot-dashed) where an inhomogeneous energy shift causes substantial broadening.

V. FERMI LEVEL SHIFT IN THE GAP, OBSERVED BY PHOTOELECTRON SPECTROSCOPY

So far the discussion has focused on empty electronic states, probed by NEXAFS. Occupied states can be probed by photoelectron spectroscopy, as shown in Fig. 4. In this case the simplest phthalocyanine dye molecule is chosen, which contains two hydrogen atoms instead of a divalent transition metal atom. We have also investigated Fe^{2+}-phthalocyanine and Fe^{3+}Cl-phthalocyanine and found qualitatively similar behavior with irradiation, i.e., a shift and a subsequent broadening of the orbitals (not shown).

The most interesting occupied state is the highest occupied molecular orbital (HOMO). It can be seen in Fig. 4 as a weak but sharp peak at 1.4 eV below the Fermi level E_F. Irradiation with soft x rays changes the position of this peak relative to E_F as quantified in the inset. The HOMO shifts upward rapidly by 0.08 eV after irradiation and stabilizes there. Prolonged irradiation broadens the HOMO peak in the photoelectron spectrum (dot-dashed spectrum in Fig. 4, bottom). This broadening is likely caused by inhomogeneous shifts. These occur probably perpendicular to the surface, due to variations in the photon flux versus depth or a depth-dependent electrostatic potential. They could also occur laterally, e.g., by charge accumulation in islands formed during thin film growth.

All the deeper molecular orbitals shift by the same amount as the HOMO, suggesting that this is an overall shift of the reference level, i.e., the Fermi level E_F. Such a shift

does not affect the optical transition energies between occupied and empty levels. That includes not only the optical transitions in the visible but also the transitions between core levels and unoccupied valence states in NEXAFS (Figs. 1 and 3).

In order to discuss the radiation-induced energy shift of the molecular orbitals, it is better to use the HOMO as the energy reference rather than the Fermi level (which is the reference in the photoelectron spectra). That makes all the molecular energy levels stationary, and only the Fermi level moves around in the HOMO-LUMO gap. It is now obvious that absorption spectroscopy does not care where the Fermi level is located within the HOMO-LUMO gap. The HOMO-LUMO gap in a molecular solid corresponds to the familiar band gap in a semiconductor.

The observed phenomenon becomes analogous to the Fermi level pinning inside the gap of a semiconductor induced by gap states, such as dopants, deep traps, defects, or interface states. Since an ideal semiconductor crystal does not contain any gap states, it is possible to shift the position of the Fermi level by introducing a very small number of gap states (down to parts per million). Such a small number of defect states is below the detection limit of photoelectron spectroscopy, but it is observed indirectly via the Fermi level shift. The energy shift saturates with increasing irradiation when the density of gap states overwhelms the density of dopants or other electrically active defects.

We can rule out charging as an alternative explanation because the observed shift is independent of the film thickness. The same charge would create different charging voltages for films with different thicknesses, i.e., different capacitances. The films were made thin enough to avoid charging. Their optical absorption was barely visible despite the high absorption coefficients of these dyes.

A radiation-induced change of the Fermi level position in the gap has consequences for the efficiency of solar cells. It can be expected to cause a change in the Schottky barrier at a semiconductor-metal interface, i.e., between a molecular solid and its metal contacts. It also is able to change the band offset at the interface between the dye and the donor/acceptor materials that separate electrons and holes. This band offset needs to be optimized in order to avoid losing energy at the interface and thereby reducing the voltage output of the solar cell.[16] The quantification of these effects would be a next step toward investigating practical solar cells by NEXAFS spectroscopy.

VI. CONCLUSIONS

In summary, we identify three mechanisms for radiation damage that need to be considered in the design of biomimetic dye molecules for solar cells:

(1) breakup of the peptide bond in the backbone of the charge-transfer protein cytochrome c,
(2) change of the 3d electron configuration and/or the crystal field at the Fe atom in the heme group of cytochrome c, and
(3) a shift in the Fermi level due to radiation-induced gap states in phthalocyanines.

True biomolecules, such as the protein cytochrome c, are much more sensitive to the effects (1) and (2) while smaller molecules that mimic the active heme center of metalloproteins are not affected. The weak links in the protein are the peptide bonds connecting the amino acids along the backbone. This result suggests that small molecules without peptide bonds might exhibit better stability in photovoltaic devices. It would be counterproductive to imitate biological molecules too closely without having a self-repair mechanism, such as that of the photosynthetic apparatus of plants.[10] This conclusion is consistent with the widespread use of small molecules in OLEDs, for example Alq_3.[28,29]

The more subtle radiation effect (3) creates a small minority of defect states, which are insignificant for the chemical composition and do not affect the absorption spectrum. They act indirectly by changing the Fermi level position via electrostatics. This is analogous to the change of the Fermi level pinning at a semiconductor interface induced by a small amount of defect states in the gap. The result is a change of the Schottky barrier at a semiconductor-metal interface or a change of the band offset at a semiconductor heterojunction. This effect saturates rather quickly and thus may be tolerable in solar cells under steady-state irradiation. The design of the dye molecule and the electron/hole collector materials in a dye-sensitized solar cell will need to take the radiation-induced Fermi level shift into account. Another option would be to heal the defects by annealing, which may happen automatically by the heat dissipated in an organic solar cell operating in bright sunlight.

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