Supplementary Materials

Bound electron enhanced radiosensitisation of nimorazole upon charge transfer

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TDDFT/ M06-2X/6-311++g(d,p) computational model was used in electronic structure calculations. All electrons have been considered explicitly for carbon, oxygen, nitrogen, hydrogen and potassium atoms with the 6-311++g(d,p) basis set

Figure caption

Figure S1: Fully optimised geometry of nimorazole at the M06-2X/6-311++g(d,p) level of theory. Fully optimized molecular structure of the K + nimorazole collisional system K−O ≈ 5.1 Å. K: yellow, O: red, C: grey, N: light blue, and H: white. Cartesian coordinates (in Å).

Figure S2: Energy (in eV) and shape of a selection of the molecular orbitals (TDDFT/ M06-2X/6-311++g(d,p)) for K + NIMO (K: purple, C: grey, N: blue, O: red, and H: white). The straight lines between the K atom and the –NO2 end in the nitroimidazole ring are just to indicate the spatial mutual position.

Figure S3: Energy (in eV) and shape of a selection of the molecular orbitals (M06-2X/6-311++g(d,p)) for NIMO (C: grey, N: blue, O: red, and H: white).
Figure S1: Fully optimised geometry of nimorazole at the M06-2X/6-311+g(d,p) level of theory. Fully optimized molecular structure of the K + nimorazole collisional system K–O ≈ 5.1 Å. K: yellow, O: red, C: grey, N: light blue, and H: white. Cartesian coordinates (in Å).

Cartesian coordinates (in Å).

| Atom | X (Å)  | Y (Å)  | Z (Å)  |
|------|--------|--------|--------|
| C    | -1.420369 | 0.935288 | -0.002623 |
| C    | -2.173875 | 1.301569 | 1.093023 |
| C    | -2.763699 | -0.681986 | 0.585502 |
| N    | -1.812232 | -0.343711 | -0.339432 |
| H    | -2.145992 | 2.245774 | 1.609137 |
| H    | -3.241564 | -1.651108 | 0.562053 |
| N    | -0.481321 | 1.677568 | -0.687116 |
| O    | -0.095453 | 2.803273 | -0.171942 |
| O    | -0.108712 | 1.352728 | -1.894973 |
| C    | -1.127140 | -1.314816 | -1.183171 |
| H    | -1.863916 | -2.060121 | -1.492879 |
| H    | -0.752059 | -0.795845 | -2.061864 |
| C    | 0.008225 | -1.982200 | -0.400485 |
| H    | 0.468590 | -2.770692 | -1.019343 |
| H    | -0.419992 | -2.467095 | 0.481591 |
| N    | 0.970923 | -0.991773 | 0.034944 |
| O    | 3.361762 | 0.290946 | 0.792860 |
| C    | 2.007597 | -0.717105 | -0.945513 |
| H    | 1.537980 | -0.493391 | -1.905521 |
| H    | 2.686518 | -1.582196 | -1.061822 |
| C    | 2.803816 | 0.495525 | -0.490399 |
| H    | 2.127998 | 1.362282 | -0.463349 |
| H    | 3.640056 | 0.686577 | -1.166570 |
| C    | 2.340919 | 0.030164 | 1.742421 |
| H    | 2.837580 | -0.109915 | 2.702912 |
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 1.660440 | 0.890794 | 1.799458 |
| C    | 1.541132 | -1.205151 | 1.354725 |
| H    | 2.199143 | -2.092655 | 1.383743 |
| H    | 0.729244 | -1.347031 | 2.073211 |
| N    | -3.010278 | 0.275255 | 1.441875 |
| K    | 0.993434 | 3.583190 | -2.269275 |
Figure S2: Energy (in eV) and shape of a selection of the molecular orbitals (VTZ/6-311G) for K + NIMO (K: purple, C: grey, N: blue, O: red, and H: white). The straight lines between the K atom and the –NO₂ end in the nitroimidazole ring are just to indicate the spatial mutual position.
LUMO+4 (0.01)  

LUMO+5 (0.23)  

LUMO+6 (0.26)  

LUMO+7 (0.38)  

LUMO+8 (0.54)  

LUMO+9 (0.60)  

LUMO+10 (0.76)  

LUMO+15 (1.32)
| LUMO+20 (1.84) | LUMO+25 (2.39) |
|----------------|----------------|
| LUMO+30 (2.93) | LUMO+35 (3.51) |
| LUMO+40 (3.94) | LUMO+45 (4.38) |
| LUMO+50 (4.81) | LUMO+55 (5.11) |
| LUMO+56 (5.20) | LUMO+60 (5.69) |
|----------------|----------------|
| LUMO+70 (7.01) | LUMO+80 (8.28) |
| LUMO+90 (9.17) | LUMO+100 (10.01) |
Figure S3: Energy (in eV) and shape of a selection of the molecular orbitals (M06-2X/6-311++g(d,p)) for NIMO (C: grey, N: blue, O: red, and H: white).

|        | HOMO-3 (-9.91) | HOMO-2 (-9.14) |
|--------|----------------|----------------|
| HOMO-1 | (-8.76)        | HOMO (-8.12)   |
|        | LUMO (-1.48)   | LUMO+1 (-0.38) |
|        | LUMO+2 (0.02)  | LUMO+3 (0.10)  |
| LUMO+4 (0.22) | LUMO+5 (0.56) |
|---------------|---------------|
| LUMO+6 (0.61) | LUMO+7 (0.63) |
| LUMO+8 (0.75) | LUMO+9 (1.00) |
| LUMO+10 (1.16)| LUMO+15 (1.66)|
LUMO+20 (2.40)  LUMO+25 (3.05)
LUMO+30 (3.54)  LUMO+40 (4.28)
LUMO+50 (5.28)  LUMO+56 (5.41)
LUMO+60 (6.68)  LUMO+70 (7.80)
| LUMO+80 (8.86) | LUMO+90 (10.03) |
|----------------|------------------|
| LUMO+100 (11.53) | LUMO+120 (17.30) |
| LUMO+140 (21.5) |