Radicals and Radical Ions Derived from Indole, Indole-3-carbinol and Diindolylmethane

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Supporting Information 1

The cartesian coordinates for all stationary points discussed in this study, as well as the detailed results of the TD-DFT calculations are in a separate text file (Supporting Information 2)

1. *Complete form of Reference 21 (Gaussian program):*

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Rev E.01, Gaussian, Inc., Wallingford CT, 2004.

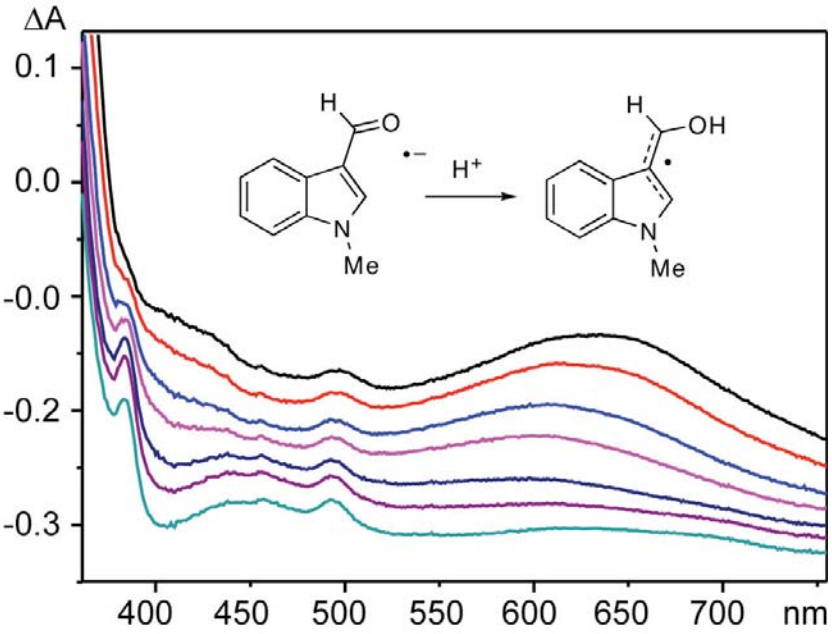

Figure S1 : Result of radiolysis of N-methyl-3-formylindole in MTHF and subsequent stepwise annealing at 95K. The first spectrum is that after bleaching of the solvated electron in MTHF, it corresponds to that of the aldehyde radical anion. The last spectrum shows the secondary products that arise on long annealing (bands at 390 and 420-480 nm).

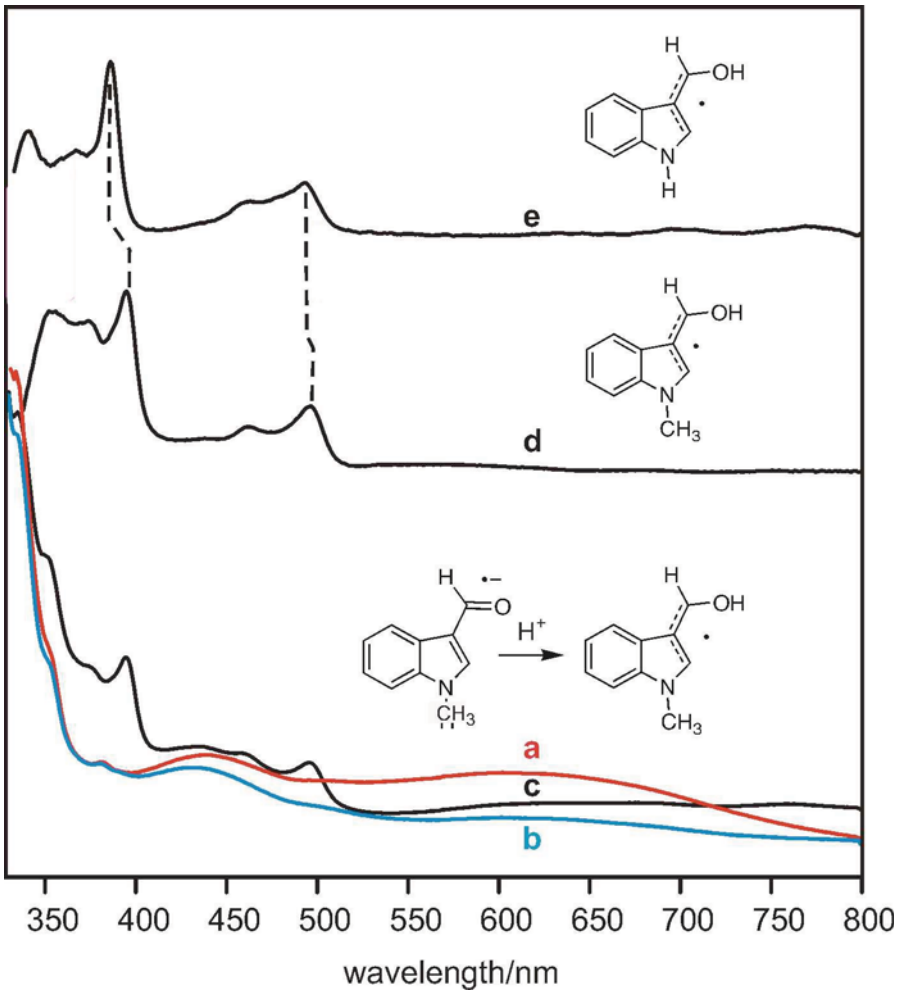

Figure S2: (a) spectrum obtained on radiolysis of N-methyl-3-formylindole **3FI** in an isopropanol glass at 77K; (b) after annealing to 135 K for 20 minutes; (c) after further annealing to 140 K for 20 minutes; (d) and (e) difference spectra showing the formation of the 500 nm band of **I3C-C•** and its N-methyl derivative, in a addition a secondary product showing a sharp peak at 390 nm

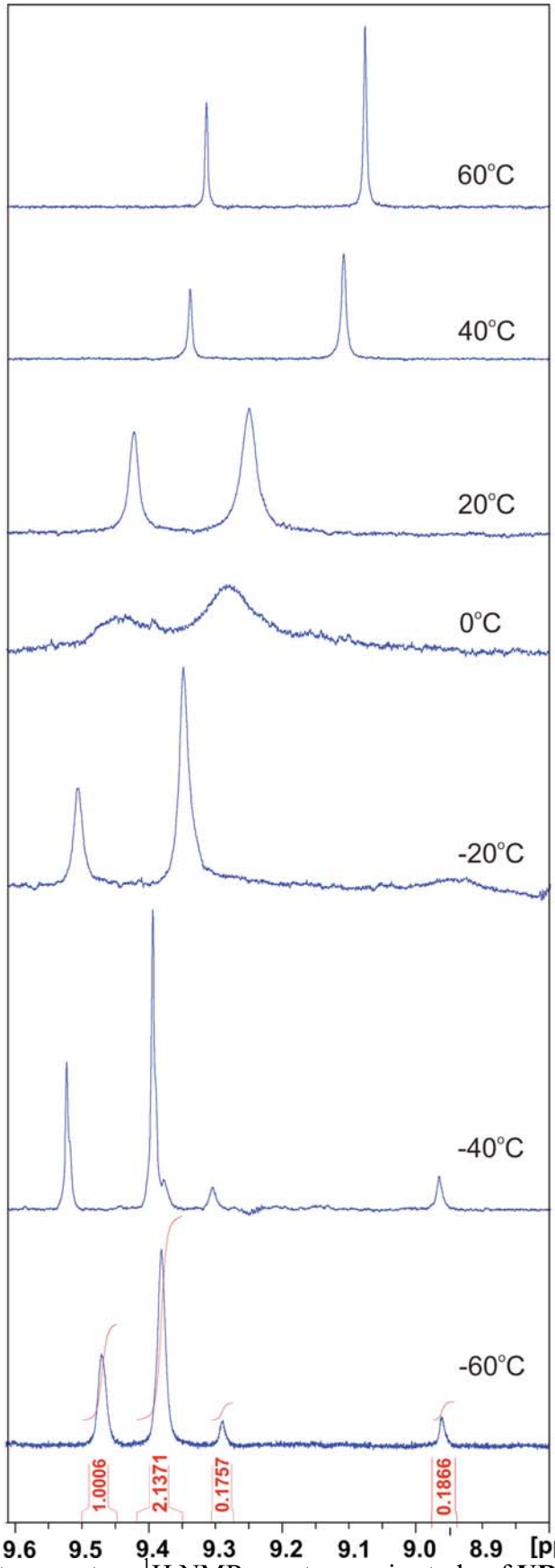

Figure S3. Variable-temperature ^{1}H NMR spectroscopic study of **URS** (region of N–H and –CH–).

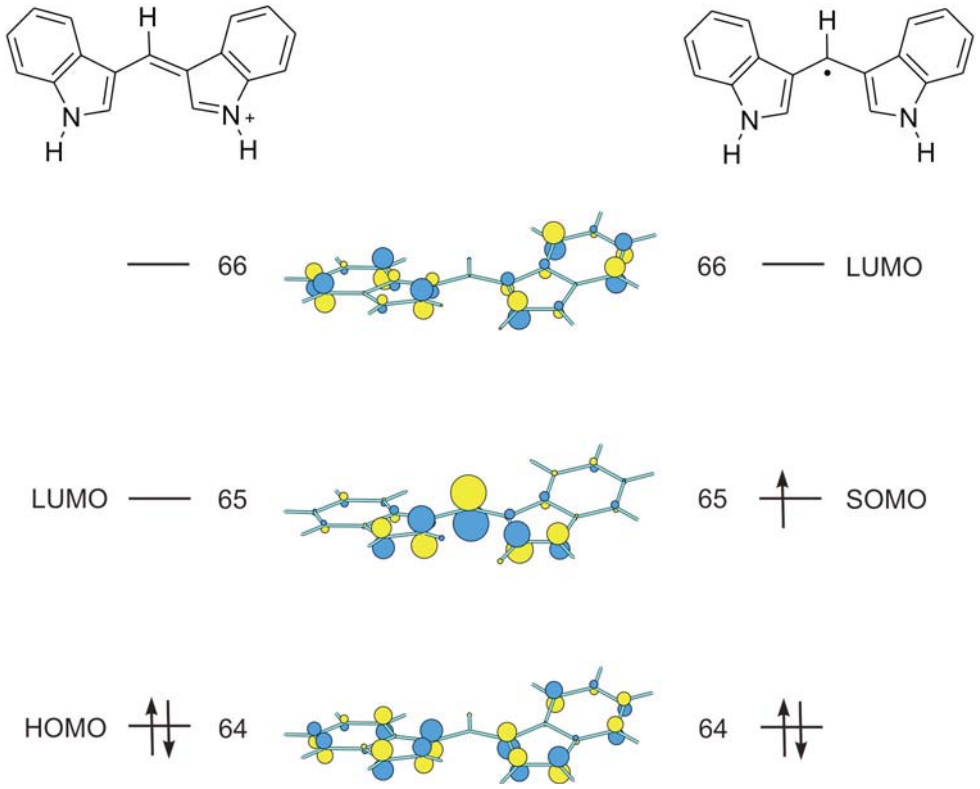

Figure S4: KS molecular orbitals involved in the electronic transitions of **URS** and **URS**$^{\bullet}$.

Table S1. Electronic structure of indole-3-carbinol radical cation **I3C**$^{\bullet+}$

Active space: 9 electrons in 10 orbitals, IPEA=0.0, imaginary shift 0.1h, 8 roots

state symmetry	*CASSCF Hartree*	*CASPT2 Hartree*	*CASPT2 nm*	*Oscillator strength*	*Reference weight*
A”	-475.2631529	-476.6094834	—	—	0.73472
A”	-475.2237807	-476.5699735	1153	$9.77 \cdot 10^{-5}$	0.73423
A”	-475.1754998	-476.5309555	580	$4.31 \cdot 10^{-2}$	0.73045
A”	-475.1281128	-476.4848575	366	$6.01 \cdot 10^{-3}$	0.73035
A”	-475.1124392	-476.4735813	335	$1.23 \cdot 10^{-1}$	0.7262
A”	-475.0771044	-476.444442	276	$1.42 \cdot 10^{-2}$	0.72464
A”	-475.0626159	-476.4270113	250	$1.96 \cdot 10^{-2}$	0.72357
A”	-475.0538915	-476.4306627	255	$1.46 \cdot 10^{-1}$	0.72256

Table S2. Electronic structure of indole-3-carbinol N-centered radical **I3C-N**$^{\bullet}$

Active space: 9 electrons in 10 orbitals, IPEA=0.0, imaginary shift 0.h1, 9 roots

state symmetry	*CASSCF Hartree*	*CASPT2 Hartree*	*CASPT2 nm*	*Oscillator strength*	*Reference weight*
A”	-474.893857	-476.245997	—	—	0.67655
A”	-474.845505	-476.200748	1007	$6.82 \cdot 10^{-5}$	0.67471
A”	-474.787564	-476.151696	483	$1.30 \cdot 10^{-2}$	0.66829
A”	-474.754137	-476.117114	354	$5.72 \cdot 10^{-2}$	0.66644
A”	-474.737106	-476.102854	318	$1.37 \cdot 10^{-2}$	0.66496
A”	-474.709994	-476.080156	275	$9.82 \cdot 10^{-4}$	0.65992
A”	-474.697452	-476.071271	261	$1.89 \cdot 10^{-2}$	0.6571
A”	-474.678426	-476.082529	279	$4.03 \cdot 10^{-2}$	0.64945
A”	-474.659944	-476.057061	241	$2.54 \cdot 10^{-2}$	0.65007

Table S3. Electronic structure of indole-3-carbinol C-centered radical, **I3C-C$^{\bullet}$**

Active space: 11 electrons in 12 orbitals, IPEA=0.0, imaginary shift 0.h1, 5 roots

state symmetry	*CASSCF Hartree*	*CASPT2 Hartree*	*CASPT2 nm*	*Oscillator strength*	*Reference weight*
A”	-474.89212	-476.24676	—	—	0.6773
A”	-474.78329	-476.15404	491	$2.72 \cdot 10^{-3}$	0.66584
A”	-474.75711	-476.12190	365	$1.39 \cdot 10^{-3}$	0.66762
A”	-474.72706	-476.10627	324	$2.50 \cdot 10^{-2}$	0.65994
A”	-474.71752	-476.09549	301	$3.18 \cdot 10^{-3}$	0.66129

Table S4. Electronic structure of 3-formylindole radical anion, **3FI$^{\bullet-}$**.

Active space :11 electrons in 12 orbitals, IPEA=0.0, imaginary shift 0.1h, 7 roots

state symmetry	*CASSCF Hartree*	*CASPT2 Hartree*	*CASPT2 nm*	*Oscillator strength*	*Reference weight*
A”	-474.30027	-475.70945	—	—	0.65945
A”	-474.22995	-475.66634	1057	$6.27 \cdot 10^{-2}$	0.6464
A”	-474.21206	-475.63168	586	$1.51 \cdot 10^{-2}$	0.65217
A”	-474.19571	-475.64427	699	$9.30 \cdot 10^{-3}$	0.6403
A”	-474.17954	-475.59780	408	$5.34 \cdot 10^{-3}$	0.651
A”	-474.15641	-475.58767	374	$3.08 \cdot 10^{-2}$	0.64295
A”	-474.13948	-475.57939	350	$4.15 \cdot 10^{-4}$	0.63714