Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unravelling Structures of Radicals of Kynurenic Acid Formed in the Photoinduced Reactions with Tryptophan and Tyrosine

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Electronic Supplementary Information

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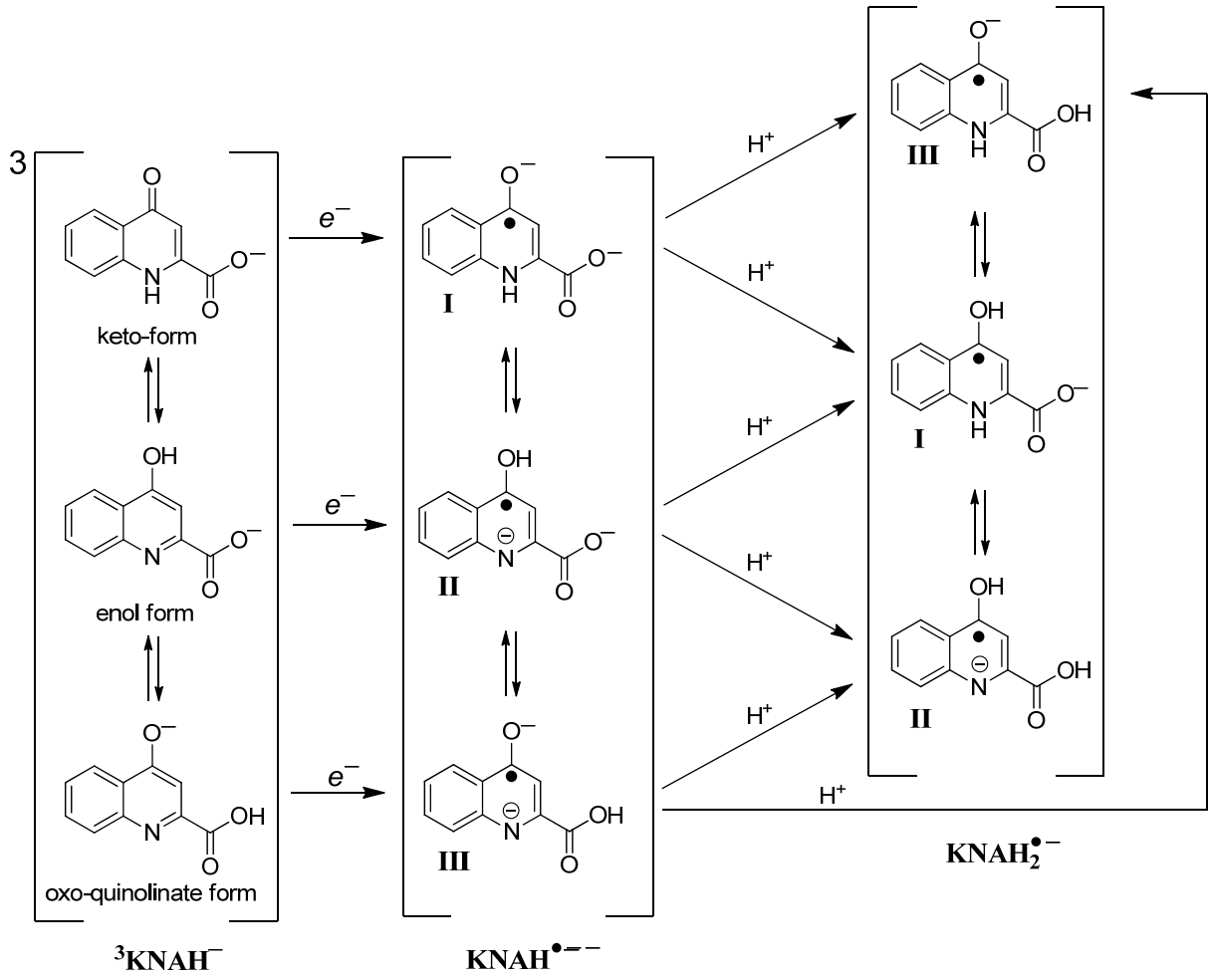
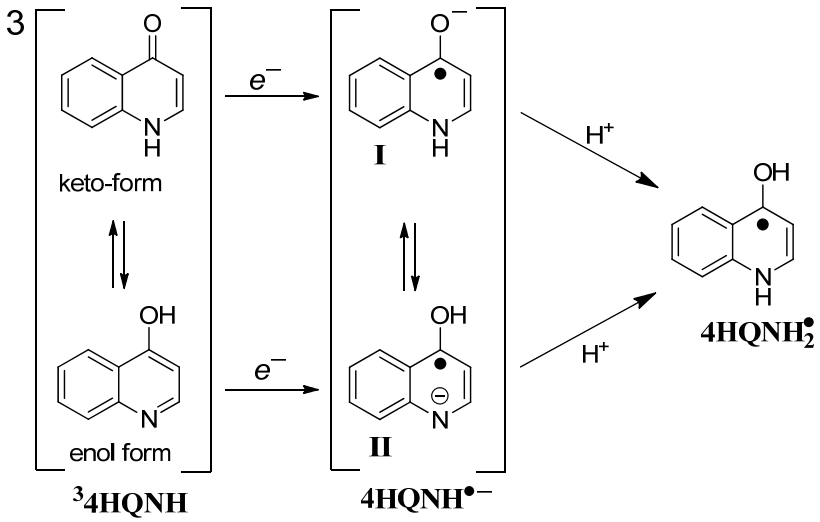


Scheme S1. Possible pathways of proton-coupled electron transfer to different tautomeric forms of triplet kynurenic acid, ^{3}KNAH$^-$, and radical structures formed so far.



Scheme S2. Possible pathways of proton-coupled electron transfer to different tautomeric forms of triplet 4-hydroxy quinolone, ^{3}4HQNH, and radical structures formed so far.

Table S1. Calculated HFCCs of 4-hydroxy quinoline (4HQN) radicals of different structures.

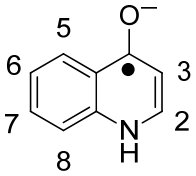
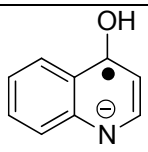
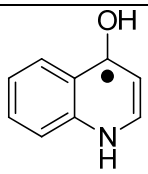
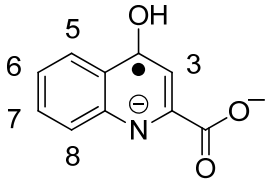
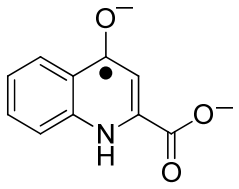
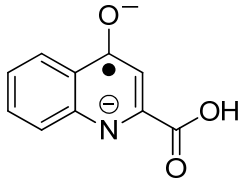
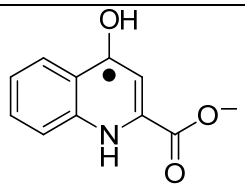
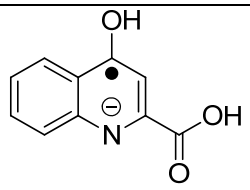
Radical		g-factor	Atom	HFCC, mT
$4HQNH^{\bullet-}$ (I)		2.00323	N1	0.108
			H1(NH)	-0.201
			H2	-0.655
			H3	0.154
			H5	-0.608
			H6	0.006
			H7	-0.395
			H8	-0.372
			H4(OH)	--
$4HQNH^{\bullet-}$ (II)		2.00295	N1	0.277
			H1(NH)	--
			H2	-0.367
			H3	-0.037
			H5	-0.591
			H6	-0.107
			H7	-0.293
			H8	-0.463
			H4(OH)	-0.067
$4HQNH_2^{\bullet}$		2.00295	N1	0.243
			H1(NH)	-0.395
			H2	-0.826
			H3	0.173
			H5	-0.440
			H6	-0.016
			H7	-0.328
			H8	-0.194
			H4(OH)	-0.124

Table S2. Calculated HFCCs of kynurenic acid (KNA) radicals of different structures.

Radical		g-factor	Atom	HFCC, mT
$KNAH^{\bullet--}$ (I)		2.00357	N1	0.100
			H1(NH)	-0.220
			H(COOH)	--
			H3	0.067
			H5	-0.295
			H6	-0.136
			H7	-0.108
			H8	-0.299
			H4(OH)	--
$KNAH^{\bullet--}$ (II)		2.00321	N1	0.286
			H1(NH)	--
			H(COOH)	--
			H3	0.127
			H5	-0.353
			H6	-0.296
			H7	-0.059
			H8	-0.473
			H4(OH)	-0.055
$KNAH^{\bullet--}$ (III)		2.00349	N1	0.196
			H1(NH)	--
			H(COOH)	-0.106
			H3	-0.178
			H5	-0.042
			H6	-0.279
			H7	0.060
			H8	-0.279
			H4(OH)	--
$KNAH_2^{\bullet-}$ (I)		2.00325	N1	0.255
			H1(NH)	-0.407
			H(COOH)	--
			H3	0.206
			H5	-0.288
			H6	-0.11
			H7	-0.176
			H8	-0.224
			H4(OH)	-0.103
$KNAH_2^{\bullet-}$ (II)		2.00339	N1	0.343
			H1(NH)	--
			(COOH)	-0.110
			H3	0.003
			H5	-0.025
			H6	-0.348
			H7	0.067
			H8	-0.338
			H4(OH)	-0.037

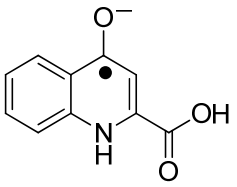
$KNAH_2^{\bullet-}$ (III)		2.00364	N1	0.129
			H1(NH)	-0.247
			H(COOH)	-0.119
			H3	-0.239
			H5	-0.065
			H6	-0.140
			H7	-0.011
			H8	-0.167
			H4(OH)	--

Table S3. Calculated HFCCs of neutral tryptophan and N-acetyl tryprophan radicals.

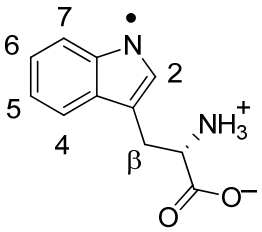
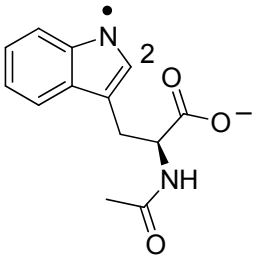
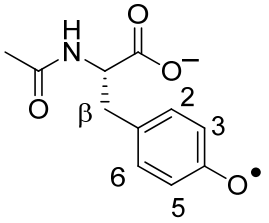
Radical		g-factor	Atom	HFCC, mT
$Trp^{\bullet}$		2.00282	N1	0.313
			H2	-0.096
			H4	-0.492
			H5	0.090
			H6	-0.425
			H7	-0.041
			β_1	1.776
			β_2	0.125
			α	0.082
N-AcTrp$^{\bullet}$		2.00284	N1	0.325
			H2	-0.108
			H4	-0.438
			H5	0.067
			H6	-0.378
			H7	-0.039
			β_1	0.866
			β_2	0.818
			α	0.214

Table S4. HFCCs of neutral N-acetyl tyrosine radical, determined utilizing the CIDNP proportionality relationship between HFCCs and CIDNP intensities detected in the photoreaction of 3,3′,4,4′-tetracarboxy benzophenone (TCBP) and N-AcTyr using the known HFCCs for TCBP radicals.[1] CIDNP spectrum is shown in Fig. S1, proportionality relationship – in Fig. S2.

Radical		g-factor	Atom	HFCC, mT
N-AcTyrO•		a	H2,6	0.13
			H3,5	-0.69
			β	0.86

[a] DFT calculations were not performed for N-AcTyr radical; in calculations of CIDNP using Adrian's model, g-factor known for Tyr radical was used, g=2.0041.[2]

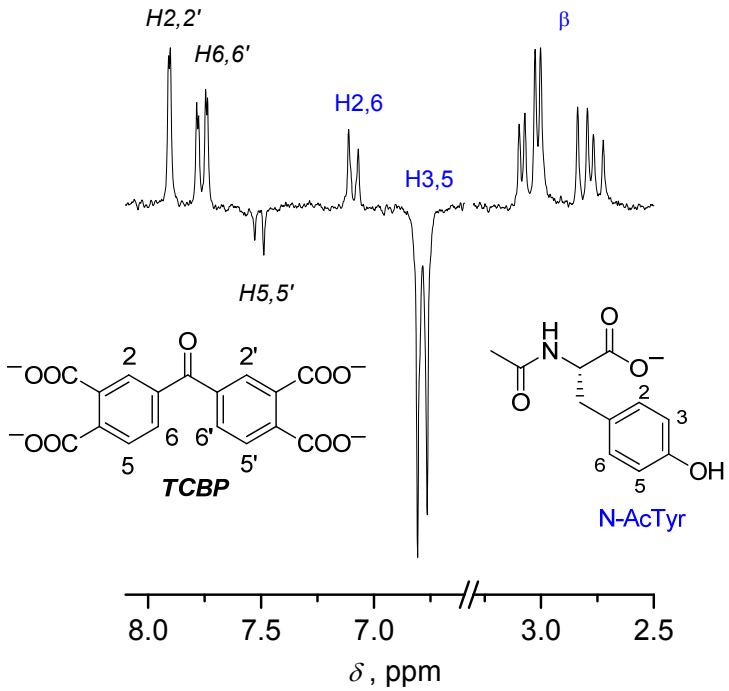


Fig. S1. 200 MHz ^{1}H CIDNP spectra, obtained in the photoreaction of 0.5 mM 3,3′,4,4′-tetracarboxy benzophenone (TCBP) and 2 mM N-acetyl tyrosine in neutral aqueous solution.

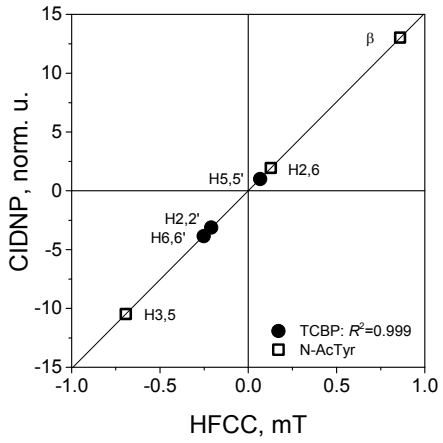


Fig. S2. Correlation between the ^{1}H CIDNP intensities of TCBP (solid circles) P_{1i} and $-P_{2j}$ of the N-acetyl tyrosine (N-AcTyr, open squares) detected in photoreaction between TCBP and N-AcTyr, and the corresponding ^{1}H HFCCs of the TCBP radicals.[1] Solid line: best fit by the function $P_{1i}=-CA_{1i}$ ($C>0$). HFCCs for neutral N-AcTyr radical (Table S4) were calculated according to the equation $A_{2j}=C^{-1}P_{2j}$ (fitting to squares).

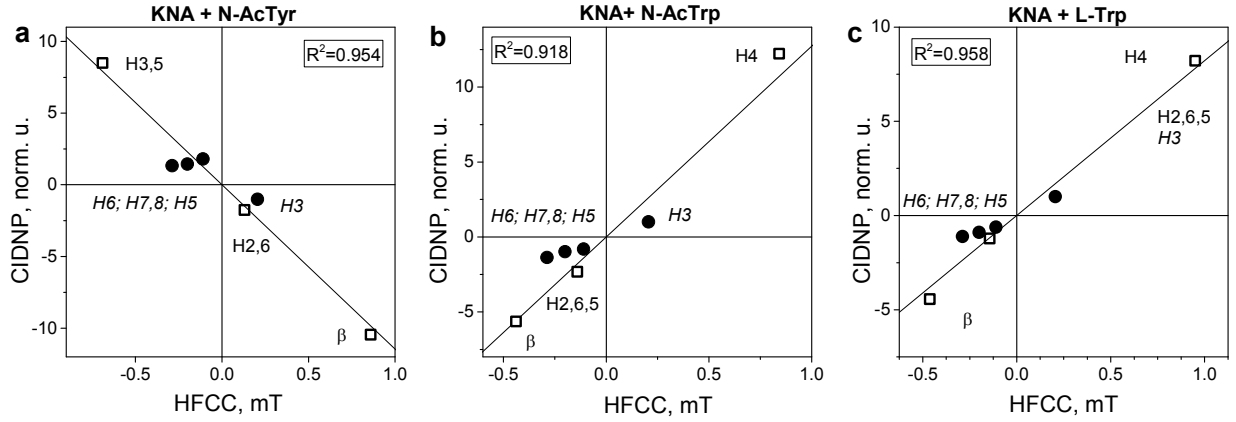


Fig. S3. Correlation between the ^{1}H CIDNP intensities P_{1i} of KNA (solid circles) and $-P_{2j}$ of the amino acid (open squares) detected in neutral aqueous solution for the photoreaction between KNA and N-AcTyr (a), N-AcTrp (b) or L-Trp (c), and the corresponding ^{1}H HFCCs of the radicals $KNAH_2^{\bullet-}$ (I) (Table S2), N-AcTyrO$^\bullet$ (Table S4), N-AcTrp$^\bullet$ (Table S3), Trp$^\bullet$ (Table S3). Solid line: best fit by the function $P_{1i}=CA_{1i}$, $P_{2j}=-CA_{2j}$.

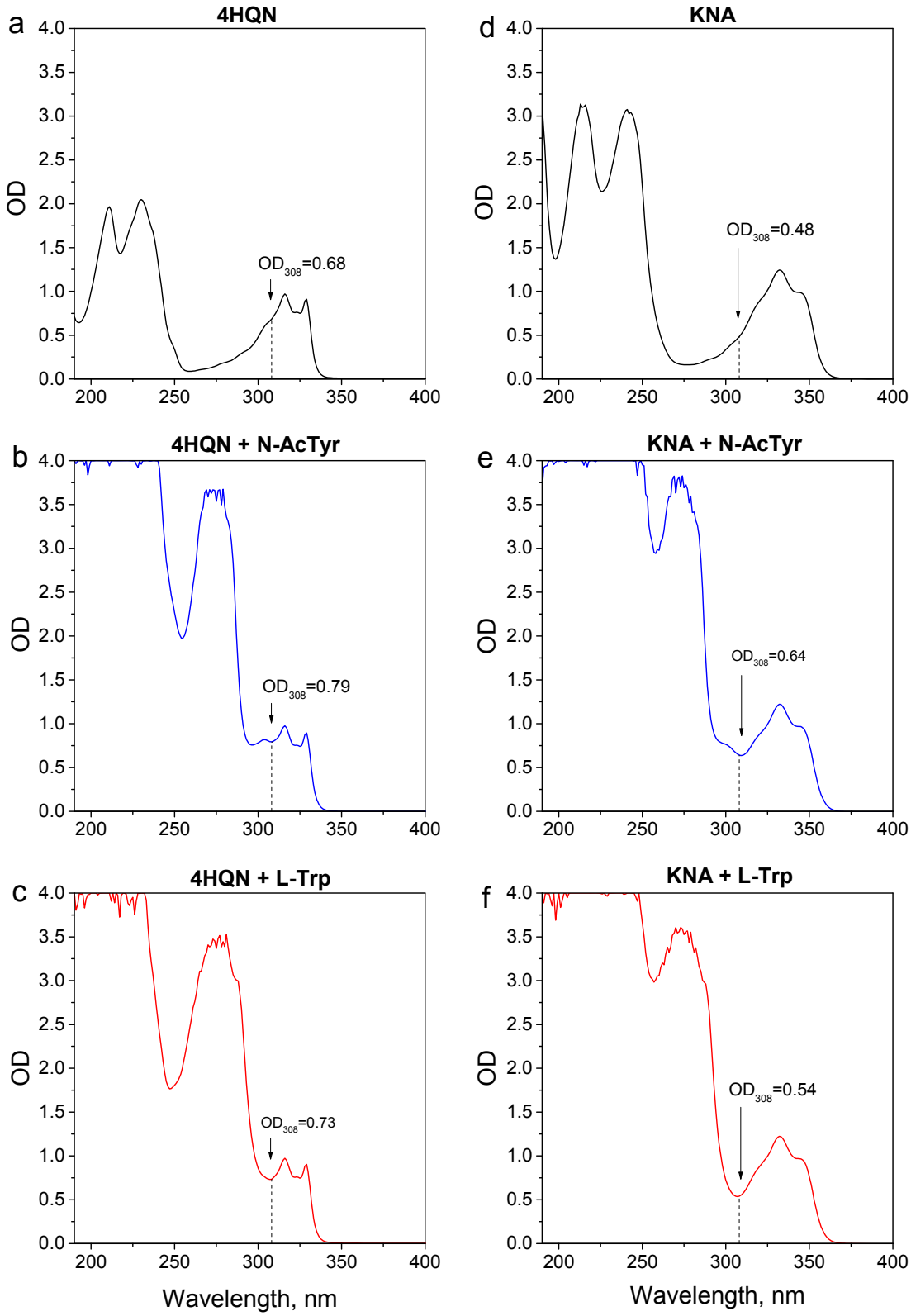


Fig. S4. Absorption spectra of neutral aqueous solutions of (a) 0.4 mM 4HQN; (b) 0.4 mM 4HQN and 20 mM N-acetyl tyrosine; (c) 0.4 mM 4HQN and 4 mM L-tryptophan; (d) 0.6 mM KNA; (e) 0.6 mM KNA and 20 mM N-acetyl tyrosine; (f) 0.6 mM 4KNA and 4 mM L-tryptophan. The optical path length was 2 mm.

References

1. O. B. Morozova, M. S. Panov, N. N. Fishman and A. V. Yurkovskaya, *Phys. Chem. Chem. Phys.*, 2018, **20**, 21127-21135.
2. M. Tomkiewicz, R. D. McAlpine and M. Cocivera, *Can. J. Chem.*, 1972, **50**, 3849-3856.