Supplement of

Exploration of the close chemical space of tryptophan and tyrosine reveals importance of hydrophobicity in CW-photo-CIDNP performances

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Table S1: Principal photo-CIDNP active known molecules. The non-exhaustive list of used photosensitizers is reported as flavin mononucleotide (FMN), bipyridyl (BIPY), fluorescein (FLUO), Atto Thio 12 (AT12), 3,3',4,4'-tetracarboxy-benzophenone (TCBP).

| Molecule               | Dye                      |
|------------------------|--------------------------|
| Tryptophan             | FMN<sup>a</sup>, BIPY, FLUO<sup>f</sup>, AT12<sup>e</sup>, TCBP<sup>e</sup> |
| NAc-tryptophan         | FMN<sup>a</sup>, TCBP<sup>e</sup> |
| 1-methyl-tryptophan    | FMN<sup>a</sup>          |
| Indole                 | FMN<sup>a</sup>          |
| NAc-serotonin          | FMN<sup>a</sup>          |
| Methoxy-tryptamine     | FMN<sup>a</sup>          |
| Tyrosine               | FMN<sup>a</sup>, BIPY, FLUO<sup>f</sup>, AT12<sup>e</sup>, TCBP<sup>e</sup> |
| 3-NO<sub>2</sub>-tyrosine | FMN<sup>a</sup>          |
| 3-F-tyrosine           | FMN<sup>a</sup>          |
| 3-amino-tyrosine       | FMN<sup>a</sup>          |
| NAc-tyrosine           | FMN<sup>a</sup>, TCBP<sup>e</sup> |
| Histidine              | FMN<sup>a</sup>, TCBP<sup>e</sup> |
| NAc-histidine          | FMN<sup>a</sup>, BIPY<sup>d</sup>, TCBP<sup>e</sup> |
| 1-methyl-histidine     | FMN<sup>a</sup>          |
| Methionine             | FMN<sup>a</sup>          |
| Adenine                | FMN<sup>b,c</sup>        |
| Guanine                | FMN<sup>b,c</sup>        |
| 3-methyl-cytosine      | FMN<sup>b</sup>          |
| 5-methyl-cytosine      | FMN<sup>b</sup>          |
| Thymine                | FMN<sup>b,c</sup>        |
| Porphyrin              | 1,4 benzoquinone<sup>c</sup> |
| polyphenol             | FMN<sup>c</sup>          |

<sup>a</sup> (Stob and Kaptein, 1989);  <sup>b</sup> (Kaptein et al., 1979);  <sup>c</sup> (Hore and Broadhurst, 1993);  <sup>d</sup> (Tsentalovich et al., 2000);  <sup>e</sup> (Saprygina et al., 2014);  <sup>f</sup> (Okuno and Cavagnero, 2016);  <sup>g</sup> (Sobol et al., 2019)
Figure S1: Polarization is dependent on the irradiation time in CW-photo-CIDNP experiments. Top: Photo-CIDNP spectra of HOPI and TRP in the presence of AT12 or fluorescein at 1 and 4 second irradiation time. The respective anomalous line intensity build up plots measured at 600 MHz $^1$H frequency are depicted in the bottom image. The spectra were measured at 0.05 mM molecule concentration. As demonstrated, the polarization is a function of the irradiation time.
Figure S2: pH dependence of the photo-CIDNP signal-to-noise enhancement for the different tryptophan analogues. A) photo-CIDNP monitored by fluorescein. B) photo-CIDNP monitored by AT12. Because the enzyme cocktail used in other
measurements to prevent dye quenching is pH sensitive oxygen scavenging was performed using a cycle of vacuum and nitrogen atmosphere flush for 30 min, that yielded however in an overall less favorable SNE.

Figure S3: Signal-to-noise enhancements (SNE) for the different tryptophan analogues at higher pH. A) AT12, pH = 9. B) fluorescein pH = 8. Because the enzyme cocktail used in other measurements to prevent dye quenching is pH sensitive oxygen scavenging was performed using a cycle of vacuum and nitrogen atmosphere flush for 30 min, that yielded however in an overall less favorable SNE. Data on the dH-TRP is missing due to lack of sufficient available sample.

Figure S4: Photo-CIDNP spectra of tyrosine (Tyr) and tyramine (TyrA), with 45° detection pulses. Zoom on the aromatics. The samples were concentrated at 100 µM of Tyr/TyrA and 25 µM of AT12.
Figure S5: Photo-CIDNP spectra of tyrosine (Tyr) and tyramine (TyrA), with 45° detection pulses. Zoom on the aliphatics. The samples were concentrated at 100 µM of Tyr/TyrA and 25 µM of AT12.
Literature

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