Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information - Luminescence Dynamics and Enhancement of the UV and Visible Emissions of Tm^{3+} in $LiYF_4$: Yb^{3+}, Tm^{3+} Upconverting Nanoparticles

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Ion	Nominal Tm^{3+} Concentration			
	0.1% Tm^{3+}	**0.2% Tm^{3+}**	**0.4% Tm^{3+}**	**0.5% Tm^{3+}**
Y^{3+}	71.12 ± 3.55%	72.15 ± 3.60%	71.68 ± 3.58%	73.80 ± 3.72%
Tm^{3+}	0.08 ± 0.00%	0.24 ± 0.01%	0.46 ± 0.02%	0.55 ± 0.03%
Yb^{3+}	28.80 ± 1.44%	27.61 ± 1.38%	27.86 ± 1.40%	25.65 ± 1.44%

Table S1 Inductively coupled plasma – mass spectrometry (ICP-MS) measured ionic concentration of Y^{3+}, Tm^{3+} and Yb^{3+} in UCNP compositions studied.

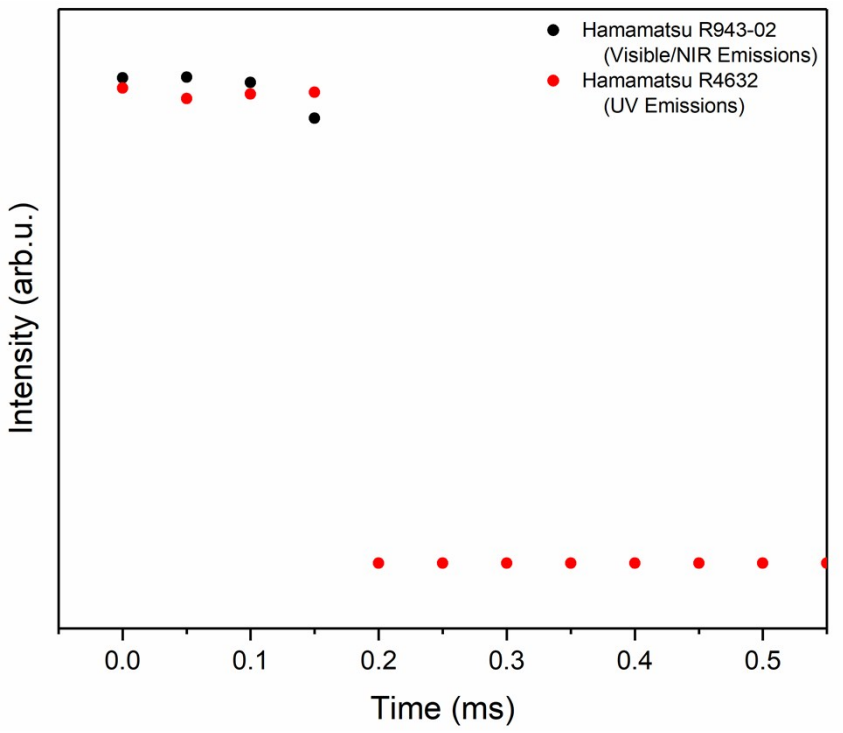

Fig. S1 Instrument response functions of the PMTs used in this work for 976 nm excitation with a 200 µs pulse width.

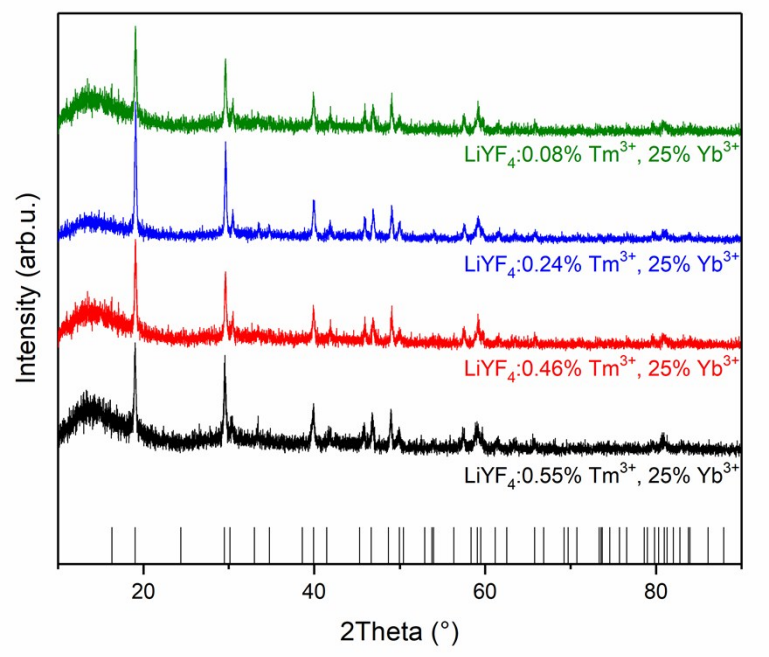

Fig. S2 Powder X-ray diffraction (PXRD) patterns for different UCNP compositions studied, compared to the theoretical pattern for the tetragonal phase with space group $I4_1/a$.[S1]

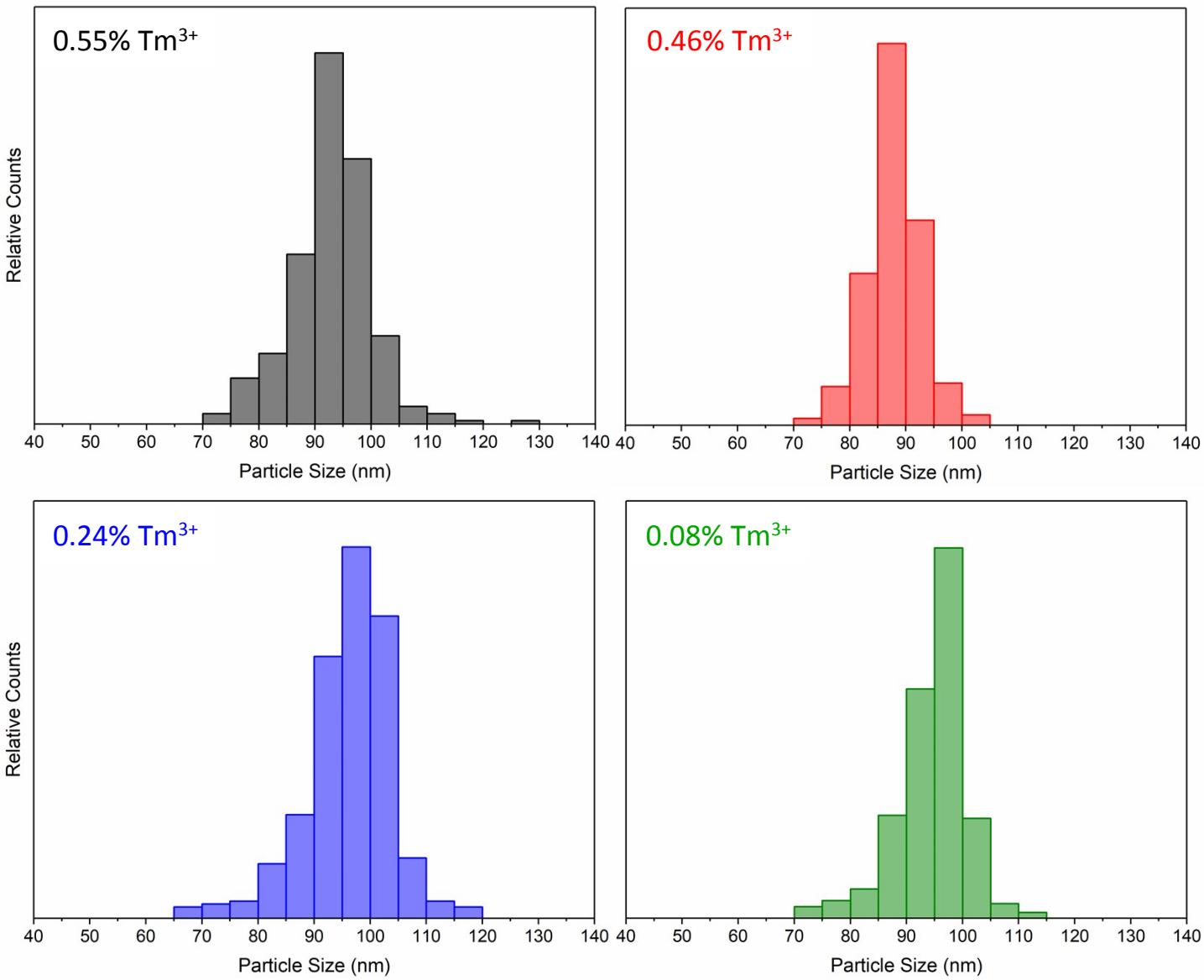

Fig. S3 Particle size distributions for the compositions studied in this work, measured from 300 nanoparticles.

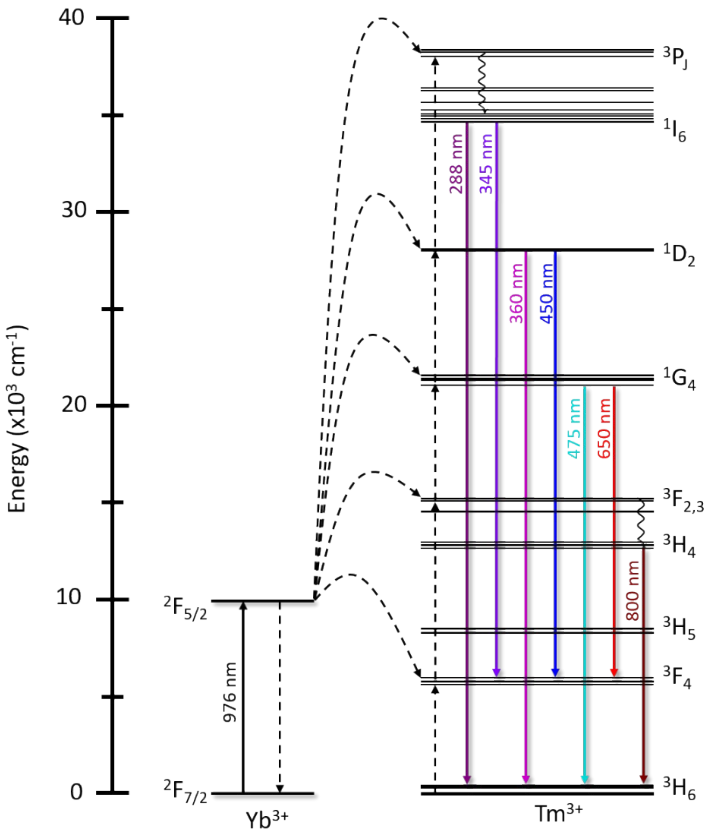

Fig. S4 Energy level diagram depicting energy transfer upconversion between Yb^{3+} and Tm^{3+}.[S2]

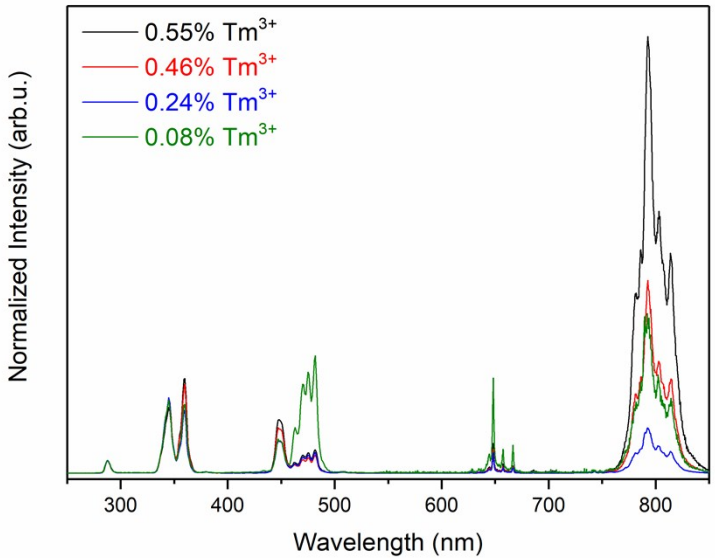

Fig. S5 Emission spectra for $LiYF_4$: 25% Yb^{3+}, x% Tm^{3+} after 976 nm excitation, normalized to the $^1I_6$ transitions.

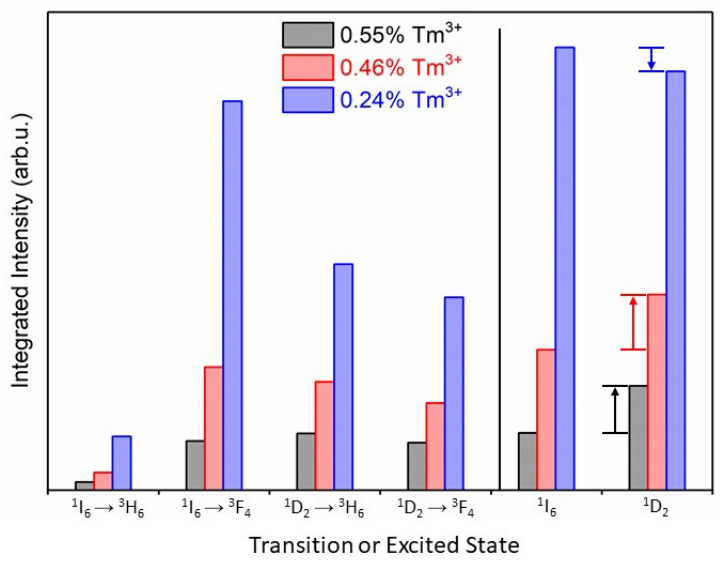

Fig. S6 Integrated emission intensities for each $^1I_6$ and $^1D_2$ transition, as well as the sum for each excited state.

Rise and Decay times were calculated using **Equations S1 and S2**, respectively.[S3,S4]

$$\tau_r = \frac{1}{I_{max}} \int_0^{I_{max}} f(t)dt \tag{S1}$$

$$\tau_d = \frac{1}{I_{max}} \int_{I_{max}}^{\infty} f(t)dt \tag{S2}$$

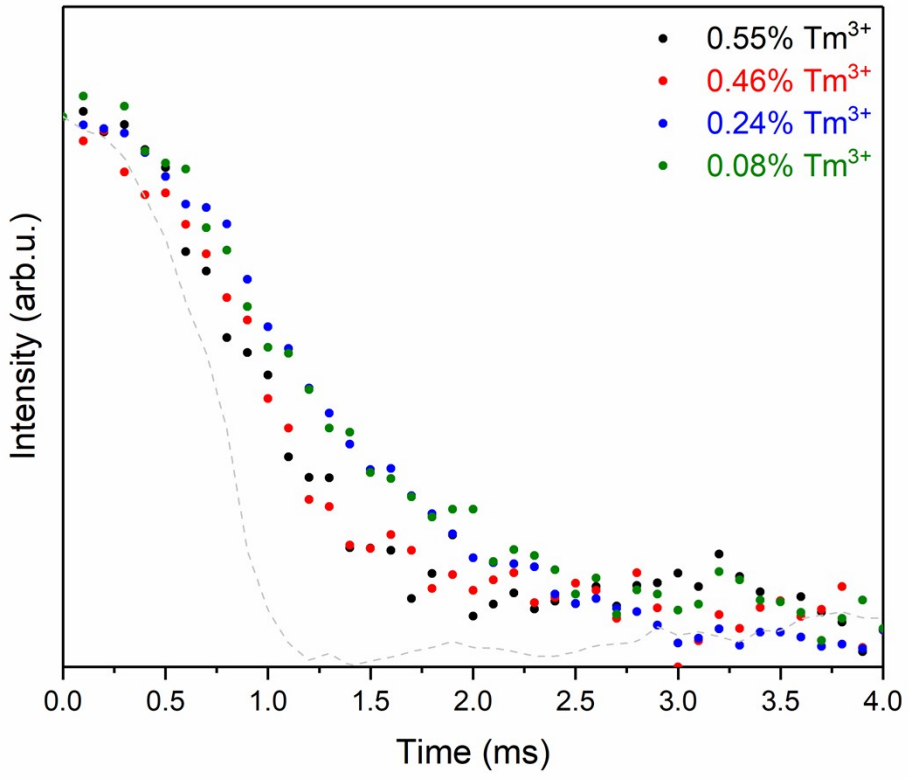

Fig. S7 Luminescence decay curves for $LiYF_4$: 25% Yb^{3+}, x% Tm^{3+} UCNPs for the Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition (1030 nm) after a pulse of 976 nm excitation. The instrument response curve is reported as a dashed gray line for reference.

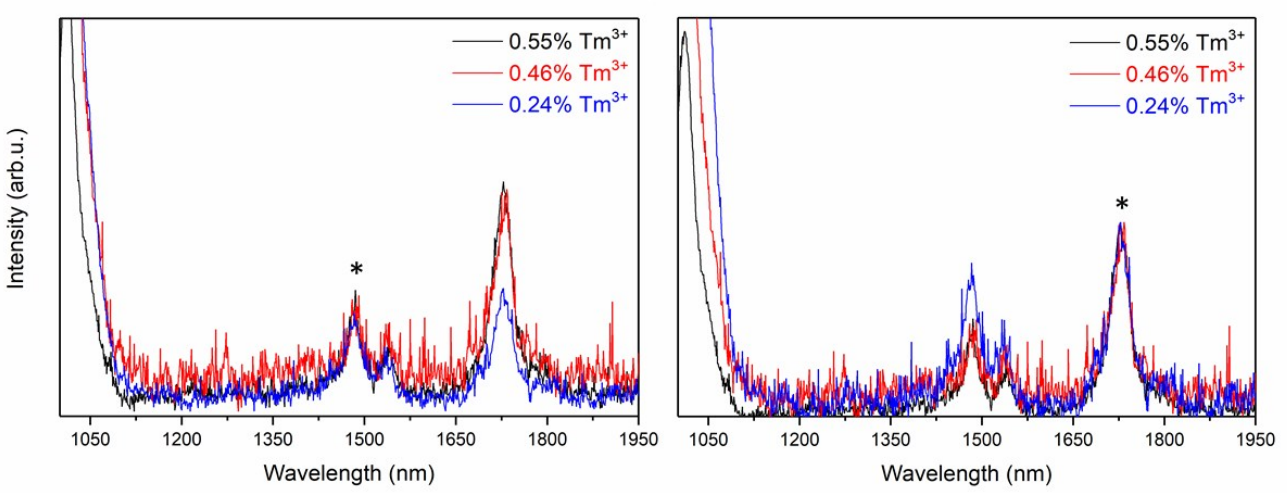

Fig. S8 NIR emission spectrum for $LiYF_4$: 25% Yb^{3+}, x% Tm^{3+} UCNPs after 976 nm excitation, normalized to the (A) $^3F_4 \rightarrow {}^3H_6$ and (B) $^3H_4 \rightarrow {}^3F_4$ emissions of Tm^{3+}, indicated by the asterisks.

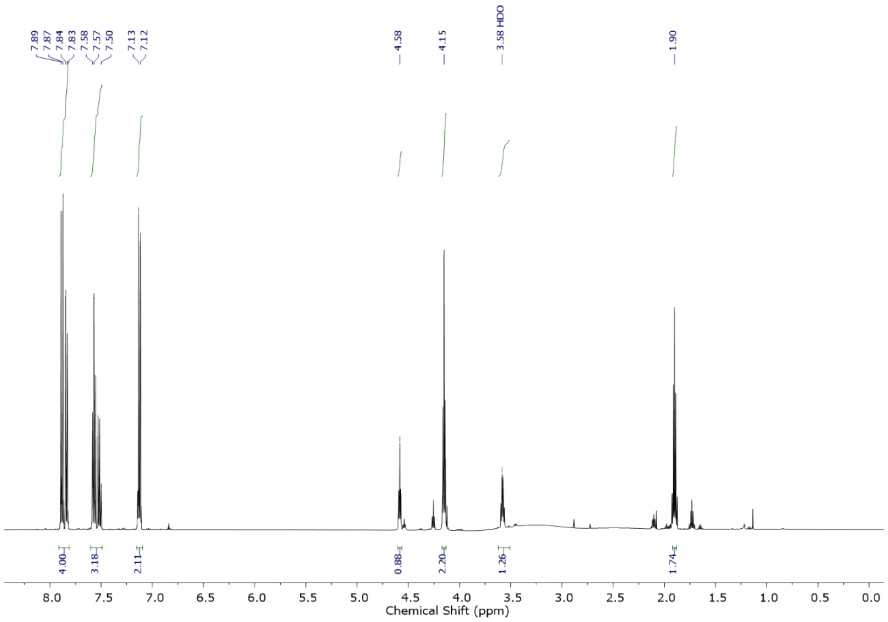

Fig. S9 ^{1}H-NMR spectrum for -3-(4-phenylazophenoxy)propanol. Resulting shifts interpreted as followed**:** 1.90 ppm (m, 2H), 3.58 ppm (m, 1H), 4.15 ppm (m, 2H), 4.58 ppm (m, 1H), 7.12 (m, 2H), 7.57 (m, 3H), 7.85 ppm (m, 4H).[S5]

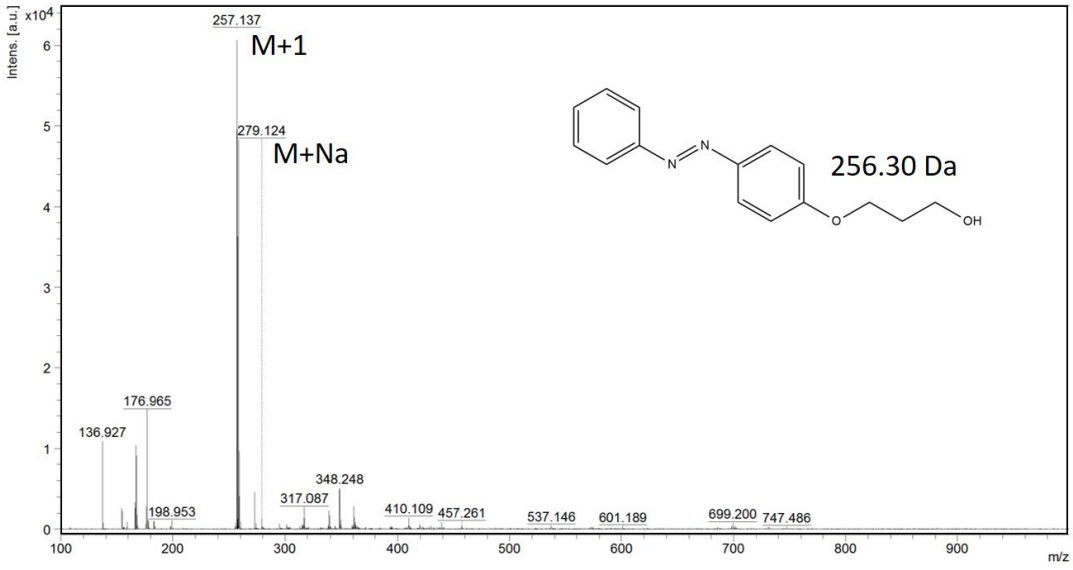

Fig. S10 Mass spectrometry results for *trans*-3-(4-phenylazophenoxy)propanol. Resulting peaks interpreted as followed: M+1 (257.137 m/z), M+Na (279.124 m/z).[S5]

References

S1. A. Braud, S. Girard, J. L. Doualan, M. Thuau, R. Moncorgé and A. M. Tkachuk, *Phys. Rev. B*, 2000, **61**, 5280–5292.

S2. V. Mahalingam, F. Vetrone, R. Naccache, A. Speghini and J. A. Capobianco, *Adv. Mater.*, 2009, **21**, 4025–4028.

S3. J. N. Demas, *Excited State Lifetime Measurements*, Academic Press, Inc., New York, 1983.

S4. S. P. Chan, Z. J. Fuller, J. N. Demas and B. A. DeGraff, *Anal. Chem.*, 2001, **73**, 4486–4490.

S5. G. A. Mandl, P. A. Rojas-Gutierrez and J. A. Capobianco, *Chem. Commun.*, 2018, **54**, 5847–5850.