

Optical Sensing of Relative Humidity via Azobenzene Photoisomerization



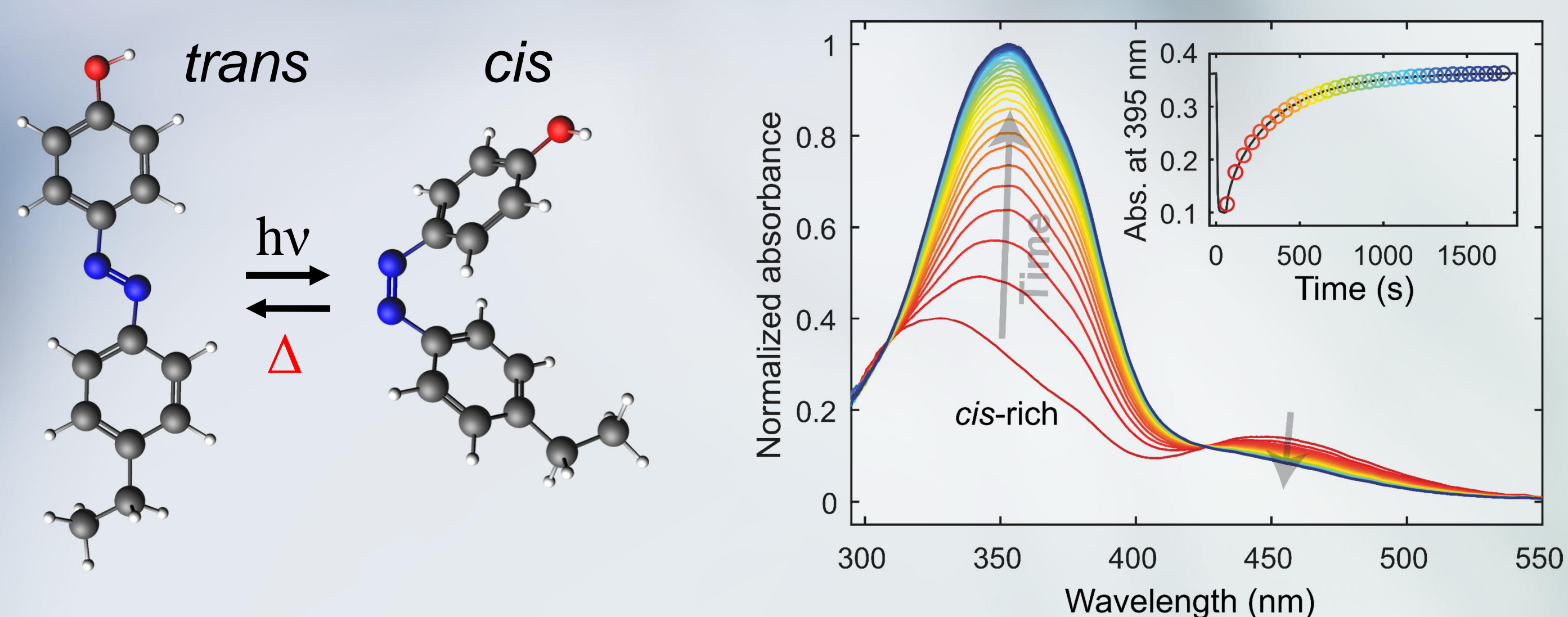
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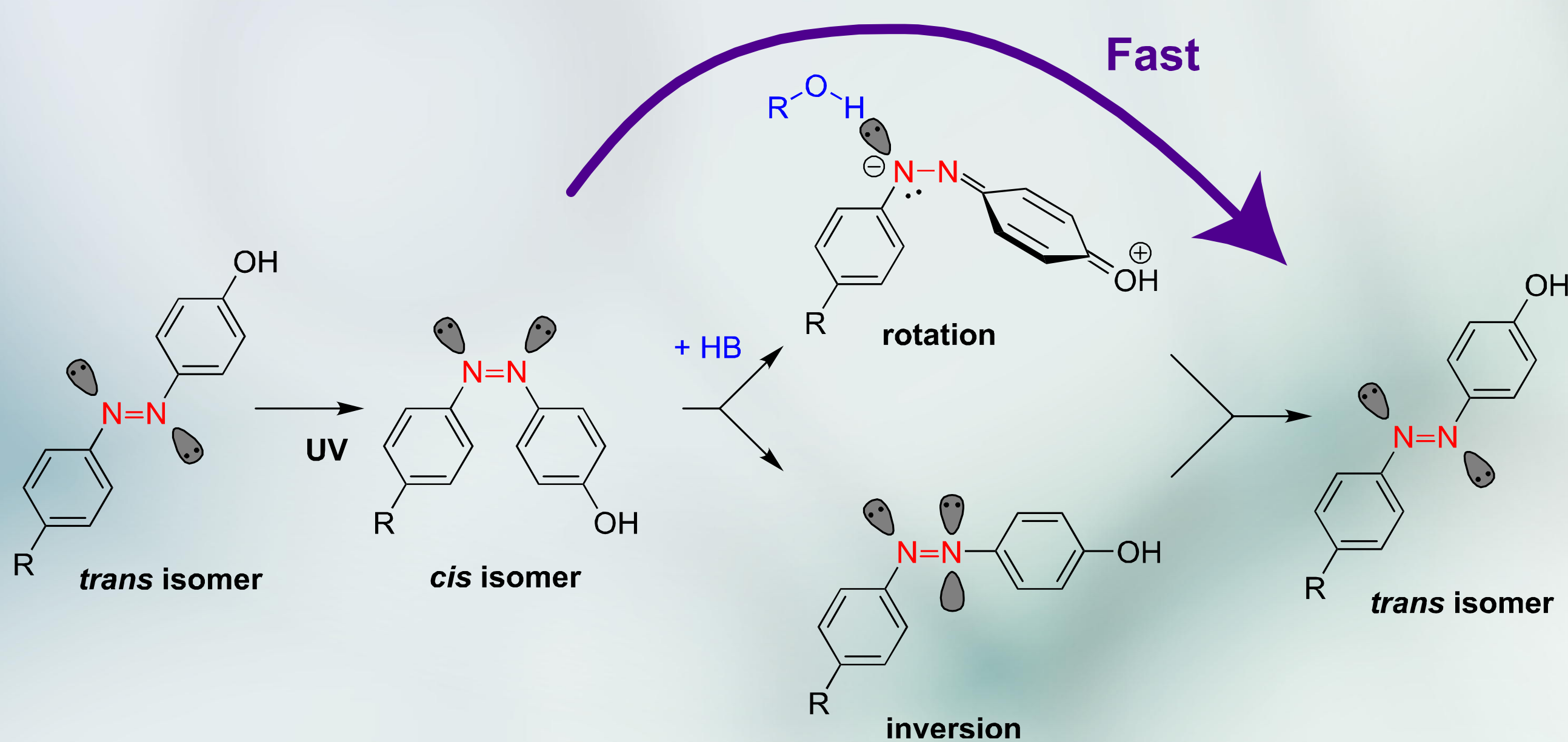
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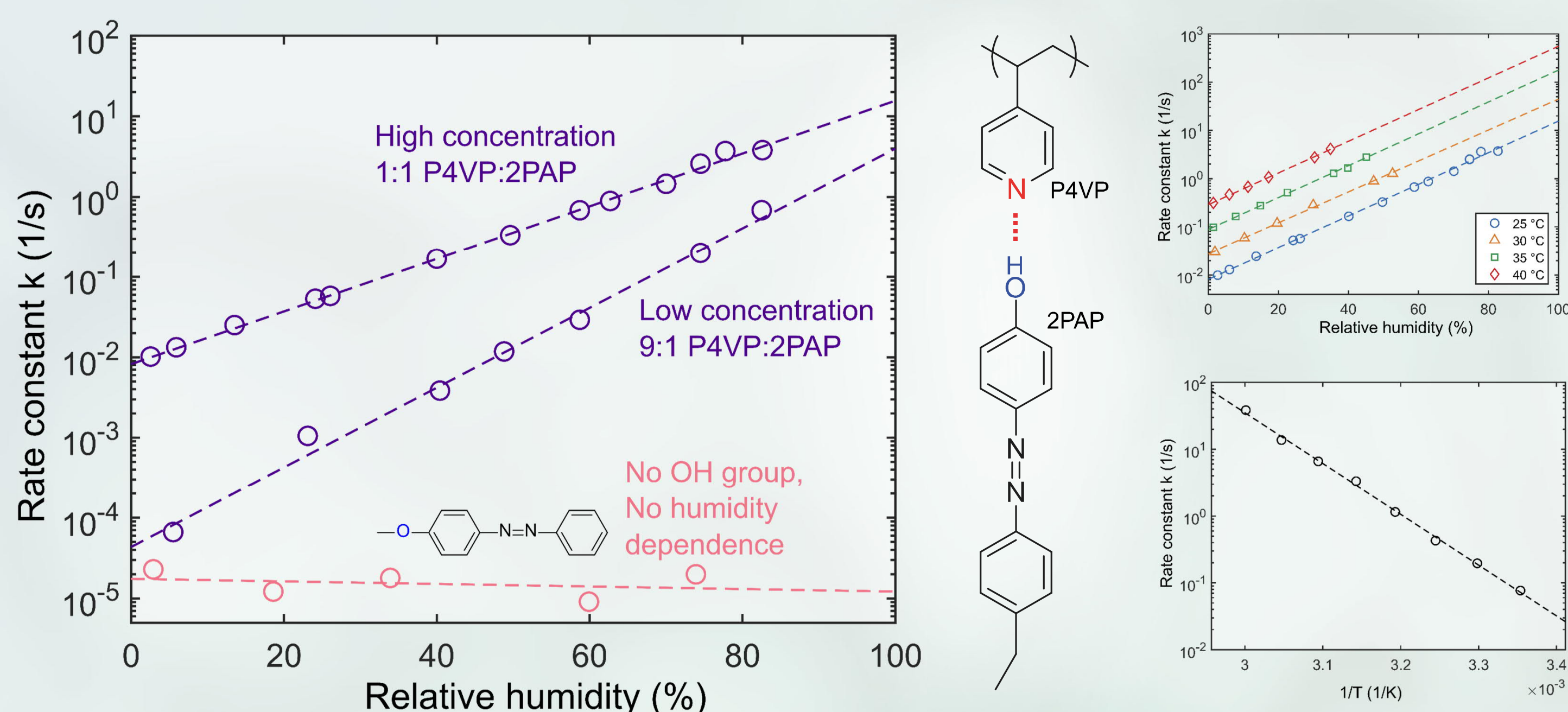
Azobenzenes isomerize with ultraviolet light from *trans* to *cis* and thermally back to *trans*. The *cis*-to-*trans* isomerization rate is strongly affected by substitution of the core azobenzene. Hydroxyazobenzenes show strong dependence of the isomerization rate on their surroundings such as the polarity of their solvent¹. We show that also in a solid supramolecular polymer with hydroxyazobenzenes, the rate is strongly dependent on the surroundings, particularly on the ambient relative humidity. Furthermore, thanks to a very systematic change of the rate constant with relative humidity, the material can be turned into a humidity sensor.



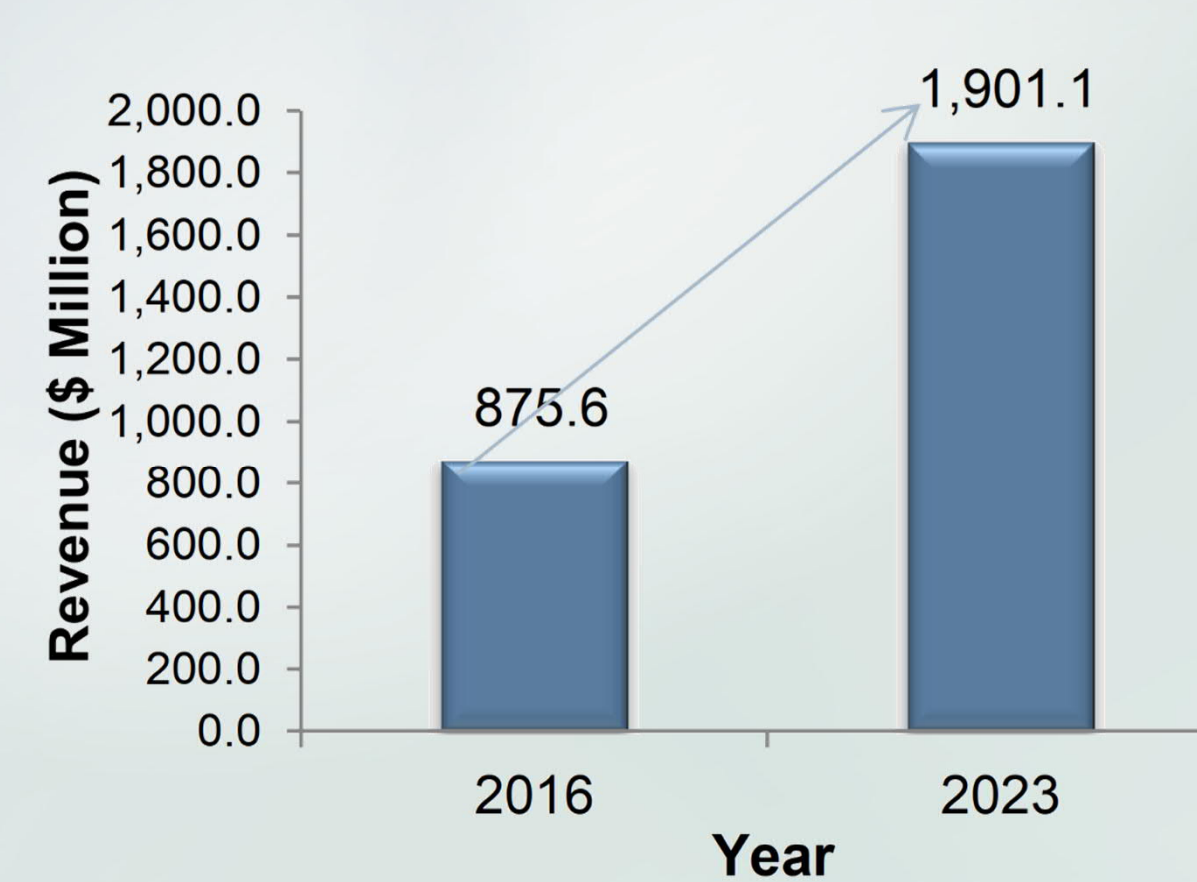
The hydroxyazobenzene isomerizes from *trans* to *cis* with photoexcitation at 360 nm causing a significant change in absorption spectrum. Isomerization from *cis* to *trans* occurs thermally and the original spectrum is fully recovered.²



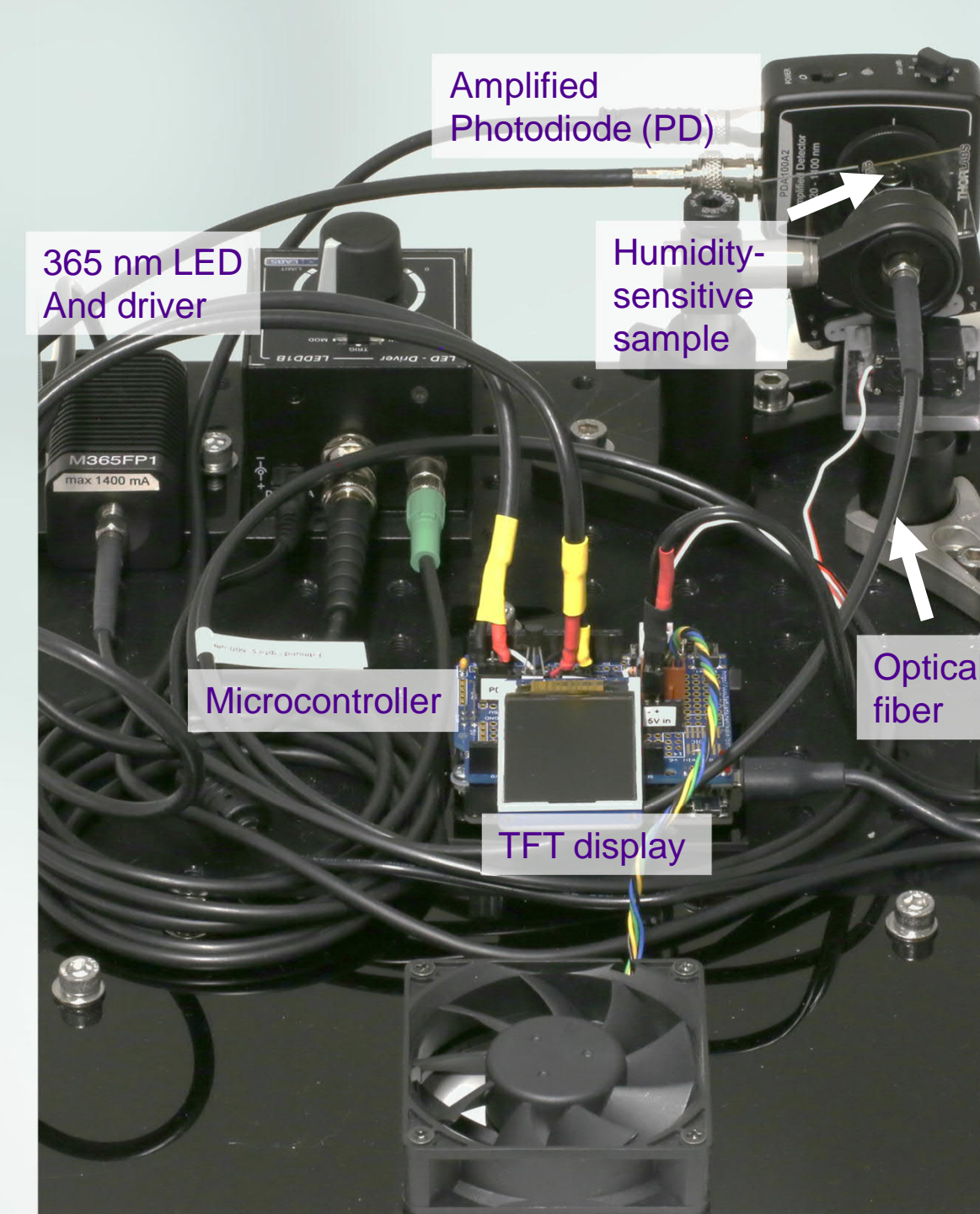
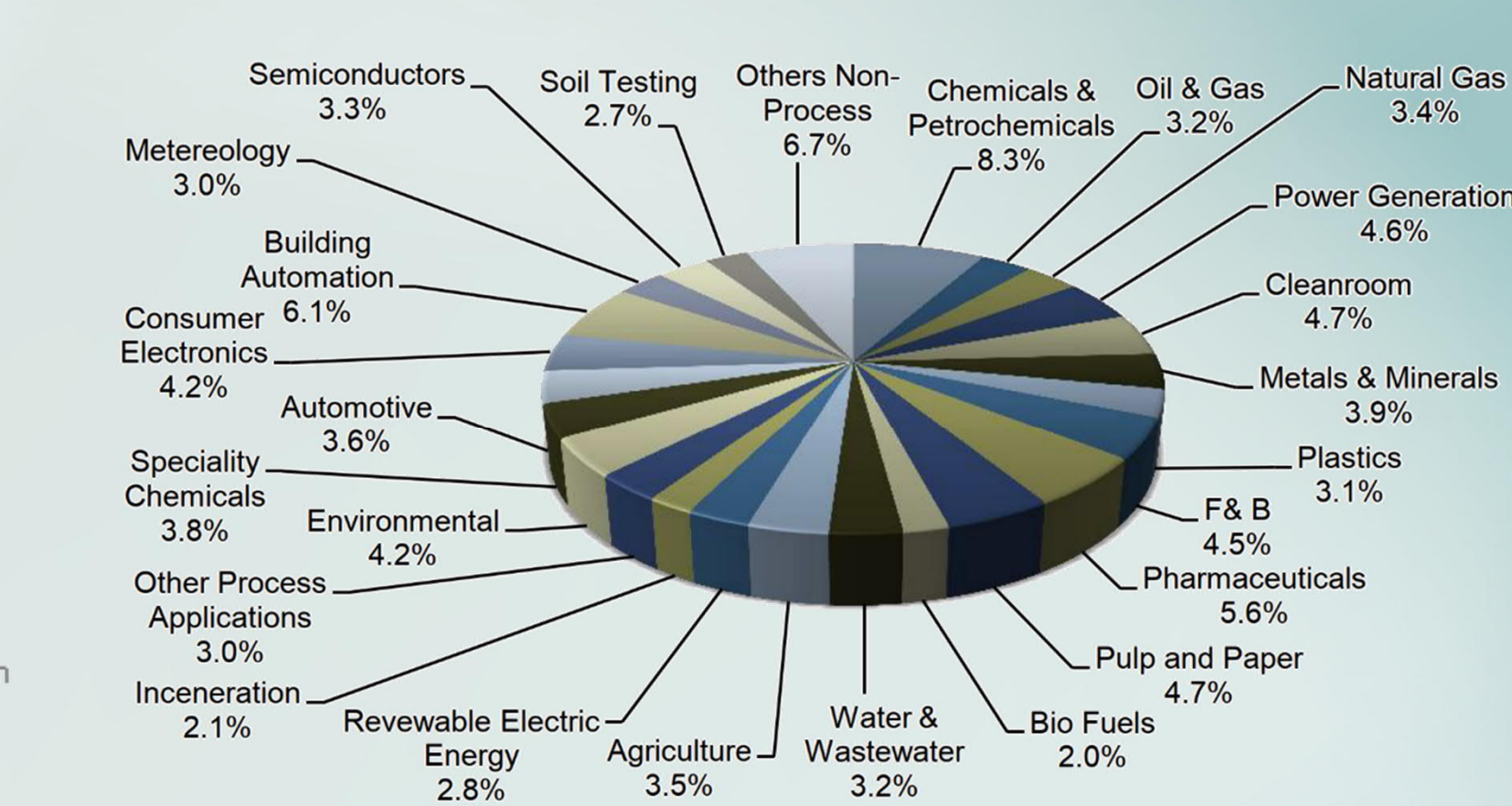
The proposed mechanism for the sensitivity of the *cis*-*trans* isomerization rate of hydroxyazobenzenes to hydrogen-bonding molecules.²



Left: Tuning of the humidity sensitivity by concentration. Middle: Molecular structure of the supramolecular polymer consisting of poly(4-vinylpyridine) (P4VP) and 4-(4-ethylphenylazo)phenol (2PAP). Right: Dependence of the rate constant on relative humidity and temperature.²



Humidity sensing market is expected to double between 2016 and 2023 while the need for humidity sensing is very scattered.³

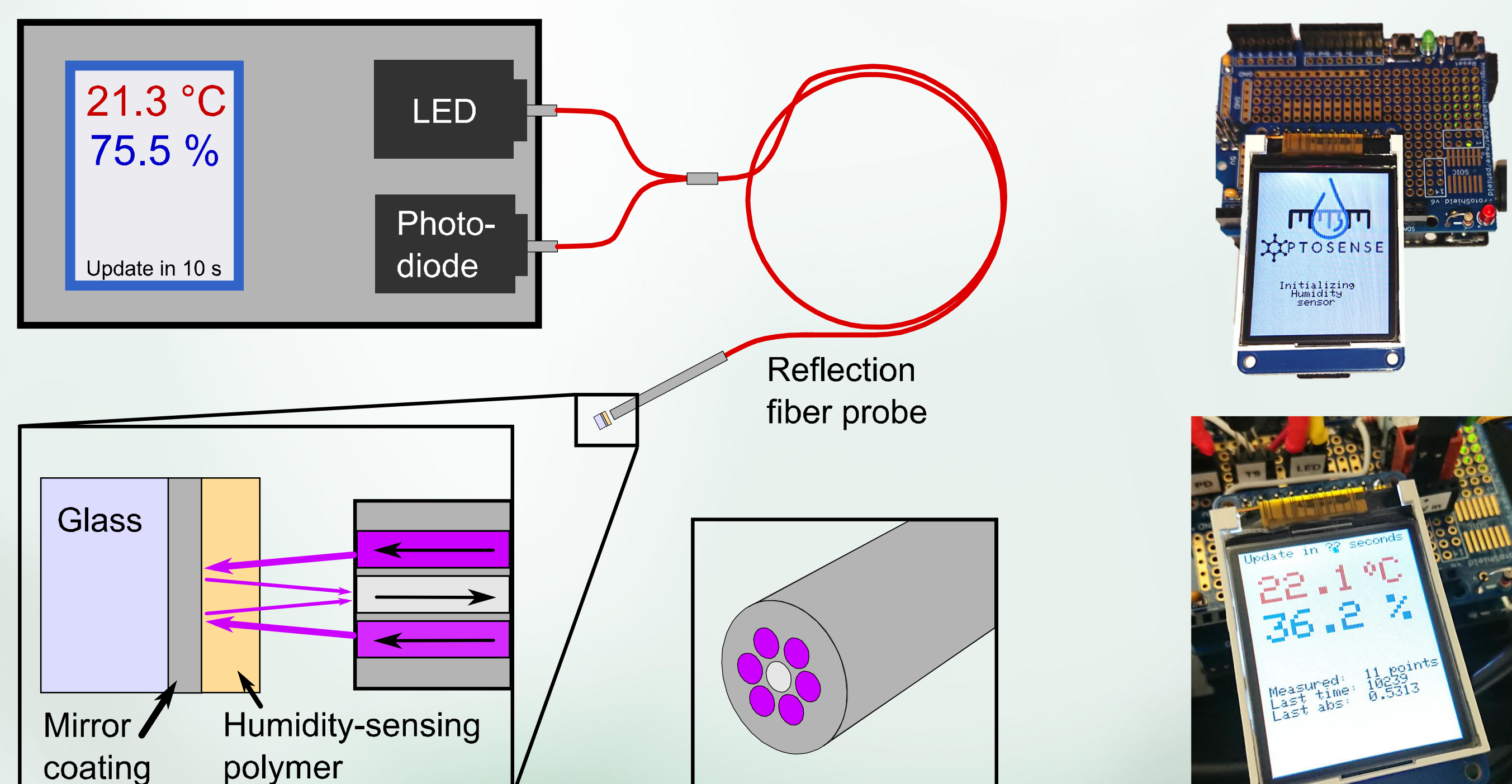


1. Measure PD signal without sample (Reference)
2. Measure PD signal without light (Dark reference)
3. Measure dark-adapted absorbance (A_{∞})
4. Illuminate for 500 ms,
5. Measure photostationary state absorbance (A_0)
6. Measure absorbance periodically: 10 ms, 20 ms, 40 ms, ... with <1 ms pulse
7. Fit for $k A(t) = -(A_{\infty} - A_0) e^{-(kt)^{\beta}} + A_{\infty}$
8. Measure temperature (T)
9. Solve for relative humidity using calibration data

$$k(T, RH) = k_0 e^{-E_a/RT} \cdot e^{\lambda \cdot RH}$$

Salt	Equilibrium RH, 20 °C	RH temperature stability	
LiCl	11.30 %	11.29 %, 10 °C	11.28 %, 30 °C
K ₂ CO ₃	43.16 %	43.14 %, 10 °C	43.17 %, 30 °C
NaCl	75.47 %	75.67 %, 10 °C	75.09 %, 30 °C

Current prototype humidity measuring device and the operation principle. Microcontroller allows standalone operation and the footprint is 30 x 40 cm.



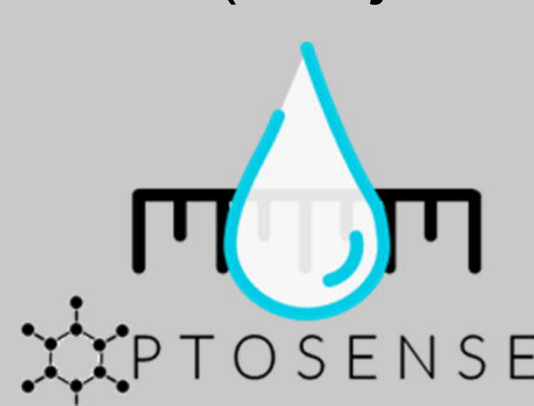
Goal of the project is a fiber-optic device that allows humidity measurement in the tip of a few-millimeter-thick reflection probe.

REFERENCES

- [1] Garcia-Amorós, J.; Sánchez-Ferrer, A.; Massad, W. A.; Nonell, S.; Velasco, D. PCCP 2010, 12, 13238–13242.
- [2] Poutanen, M.; Ahmed, Z.; Rautkari, L.; Ikkala, O.; Priimagi, A. ACS Macro Lett. 2018, 7, 381–386.
- [3] Frost & Sullivan, Global Humidity and Moisture Sensors Market, Forecast to 2023 (2017).

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