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Thermal Isomerization of Hydroxyazobenzenes as a Platform for Vapor Sensing

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S Supporting Information

ABSTRACT: Photoisomerization of azobenzene derivatives is a versatile tool for devising light-responsive materials for a broad range of applications in photonics, robotics, microfabrication, and biomaterials science. Some applications rely on fast isomerization kinetics, while for others, bistable azobenzenes are preferred. However, solid-state materials where the isomerization kinetics depends on the environmental conditions have been largely overlooked. Herein, an approach to utilize the environmental sensitivity of isomerization kinetics is developed. It is demonstrated that thin polymer films containing hydroxyazobenzenes offer a conceptually novel platform for sensing hydrogen-bonding vapors in the environment. The concept is based on accelerating the thermal *cis−trans* isomerization rate through hydrogen-bond-catalyzed changes in the thermal isomerization pathway, which allows for devising a relative humidity sensor with high sensitivity and quick response to relative humidity changes. The approach is also applicable for detecting other hydrogen-bonding vapors such as methanol and ethanol. Employing isomerization kinetics of azobenzenes for vapor sensing opens new intriguing possibilities for using azobenzene molecules in the future.
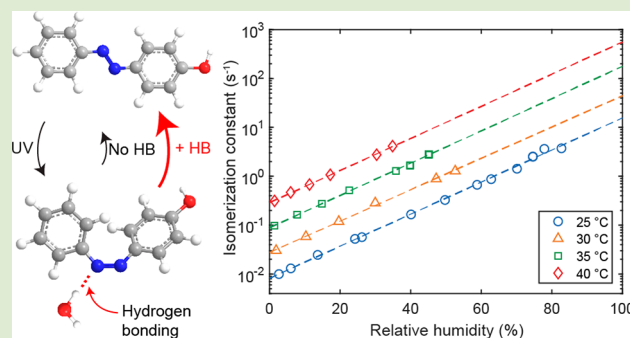
Photoswitchable and photochromic compounds provide a unique platform for devising stimuli-responsive materials whose function and properties can be remotely manipulated with light, with high spatiotemporal resolution.[1] Their light sensitivity stems from photoinduced changes in molecular conformation and electronic properties, which in recent years have been extensively utilized in applications ranging from optical memories[2,3] and light-to-mechanical energy conversion,[4,5] to photocontrol of chemical reactions[6] and biological functions.[7,8] The utility of photoswitchable materials can be further expanded if the materials are multiresponsive, that is, their optical response can be tuned via changes in environmental conditions (e.g., humidity, pH, presence of analytes). This offers a conceptual basis for photochromic sensors,[9,10] which have been developed from diarylethenes and spiropyrans, for example, for sensing anions,[11] amines,[12] and thiols.[13] For azobenzenes, to the best of our knowledge, such an isomerization kinetics based concept has not been demonstrated.

Azobenzenes are a particularly versatile class of photoswitchable compounds, as they exhibit two isomeric states, *trans* and *cis*, with a large difference in geometry, absorption spectra, and dipole moment. The power of azobenzenes lies in the fact that the lifetime of the metastable *cis*-isomer can be controlled over a wide range, from milliseconds in push−pull azobenzenes[14] up to even several months in *ortho*-substituted

azobenzenes.[15] While fast thermal relaxation is useful in, for example, optical switching[16] and the long-lived *cis*-state desired in photobiology,[17] azobenzene derivatives whose thermal isomerization dynamics depends strongly on the environmental conditions are particularly interesting. As the most prominent example, 4-hydroxyazobenzenes can experience a change of up to 5 orders of magnitude in the *cis*-lifetime in nonpolar versus polar solvents due to hydrogen-bond-assisted tautomerization.[14,18] The photochemistry of hydroxyazobenzene derivatives has been comprehensively studied in solutions.[19−21] In the solid state, they have been utilized as building blocks for supramolecular self-assemblies[22−24] and photoactive units in light-responsive polymer systems.[25] However, none of these studies makes use of the huge "dynamic range" in the isomerization kinetics of hydroxyazobenzenes, which has been largely disregarded in the solid state.

Herein, we show that the isomerization kinetics of 4-hydroxyazobenzenes in a polymeric environment offers an excellent, conceptually novel platform for sensing hydrogen-bonding vapors. More precisely, we devise and characterize a relative humidity sensor, which is fast, reliable, and accurate. We also demonstrate sensitivity to other hydrogen bonding
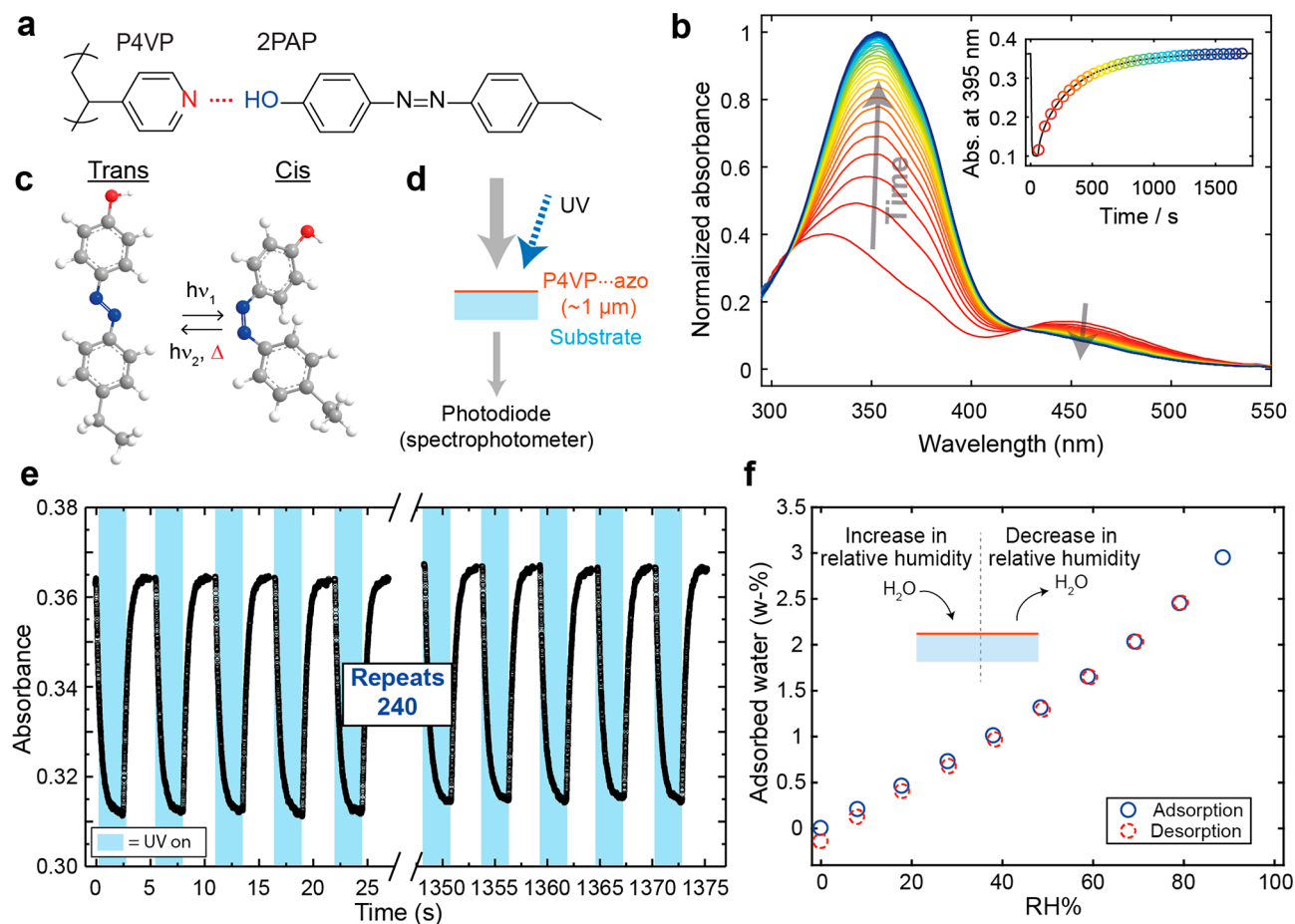
Figure 1. (a) Supramolecular, nominally stoichiometric complex of poly(4-vinylpyridine) (P4VP) and 4-(4-ethylphenylazo)phenol (2PAP). (b) Spectral changes of a thin film of nominally equimolar P4VP(2PAP) complex after UV irradiation. Inset: thermal *cis*−*trans* relaxation of the same sample. (c) *Trans*- and *cis*-isomers of 2PAP. (d) Simplified schematic representation of the experimental geometry. The gray and blue arrows indicate white probe light and UV pump light, respectively. (e) An example of the reproducibility of the thermal isomerization over 250 pumping−relaxation cycles. (f) Adsorption and desorption isotherms of water at 25 °C for the equimolar P4VP(2PAP) complex.

vapors, such as methanol and ethanol, and outline the possibility for monitoring several hydrogen-bonding vapors, or vapor content and temperature, simultaneously. We believe to propose a completely new way of using azobenzene-containing photoresponsive polymers for sensing vapors.

Relative humidity (RH) is generally measured either by capacitive or resistive sensors, and a large variety of different sensors having electrical or optical readouts have been built.[26−28] The majority of the sensors are based on adsorption of water molecules from the gaseous environment to an active sensing material where it changes permittivity or conductivity or induces swelling, translating into the readout signal. These sensors often measure an extrinsic property of the sensory material, which is dependent on the exact geometry, that is, needs device-specific calibration. In contrast, our sensor concept relies on isomerization kinetics, which is an intrinsic material property. Therefore, the exact geometry is irrelevant and no device-specific calibration is needed, which is a significant benefit compared to the commercial devices.

As depicted in Figure 1a, we use 4-(4-ethylphenylazo)-phenol (2PAP) embedded into a solid poly(4-vinylpyridine) (P4VP) matrix. P4VP and 2PAP form hydrogen-bonded supramolecular complexes, allowing high 2PAP loading to be used without phase separation: thin films of P4VP(2PAP) remain amorphous and of high optical quality, even at a nominally equimolar

complexation ratio, corresponding to 80 wt % azobenzene concentration.[29] Upon UV (365 nm) irradiation, the 2PAP molecules undergo efficient *trans*−*cis* isomerization in the solid state, as illustrated by the spectral changes shown in Figure 1b (Figure 1c displays the *trans*- and *cis*-isomers of 2PAP). The samples are thin films (~1 μm) on glass/quartz substrates and the spectral changes are measured in transmission (Figure 1d). The spectral changes are typical to azobenzene derivatives: the $\pi−\pi^*$ transition centered at 352 nm decreases significantly upon UV illumination, while the $n−\pi^*$ transition at 450 nm strengthens, indicating efficient *trans*−*cis* isomerization.

The inset of Figure 1b displays the thermal *cis*−*trans* isomerization of the 2PAP molecules in the P4VP matrix. In liquids and in polymers above glass transition temperature (T_g), the thermal isomerization typically follows simple first-order kinetics. However, it turns out that a stretched exponential function, that is, Kohlrausch−Williams−Watts function, explains better our findings:

$$A(t) = (A_0 - A_\infty)e^{-(kt)^\beta} + A_\infty \qquad (1)$$

where A_0 is the absorbance after illumination, A_∞ is the absorbance of the fully relaxed, that is, all-*trans*, state, β is the stretching exponent, and k is the rate constant of thermal isomerization. In fact, this is not surprising, as the stretched exponential function is known to explain, for example, glassy
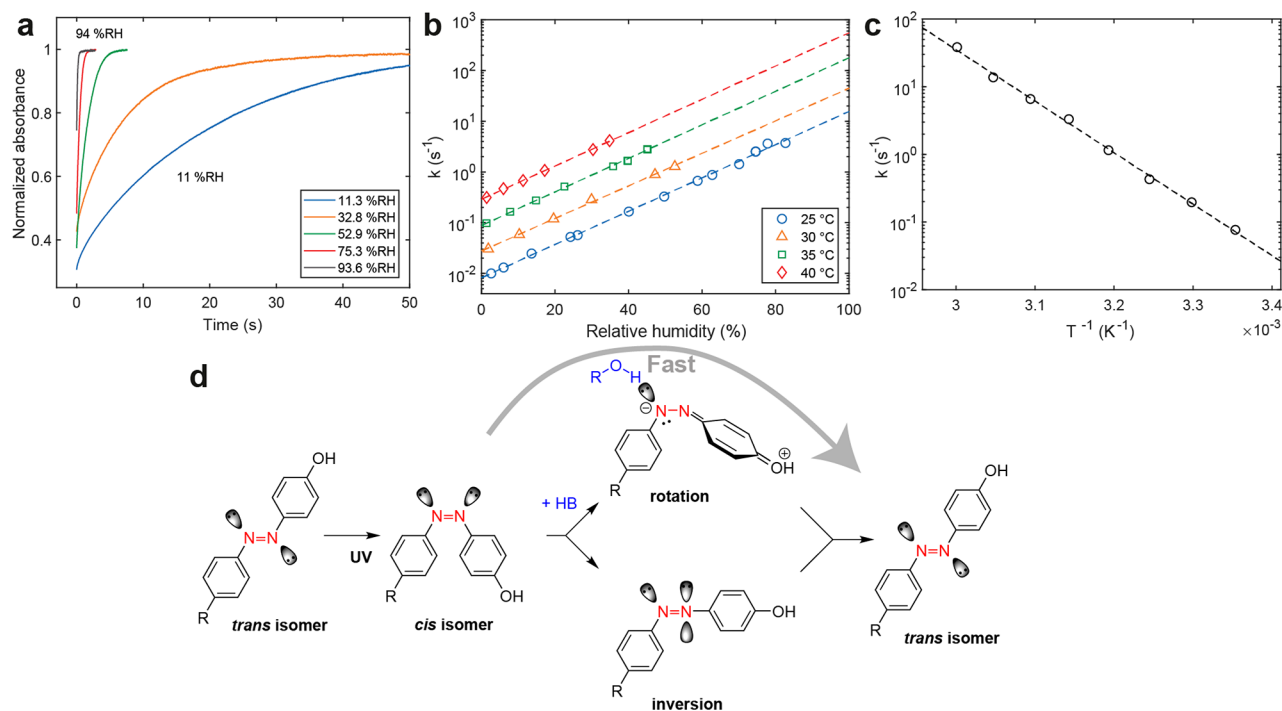
Figure 2. Relative-humidity dependence of thermal isomerization of a thin film of nominally equimolar P4VP(2PAP) complex. (a) Thermal isomerization curves at different RH values. (b) Rate constants of the *cis*−*trans* isomerization at different RH values at different temperatures. (c) Arrhenius-type temperature dependence of the rate constant of thermal isomerization measured at 30% RH. (d) Proposed mechanism for the sensitivity of the isomerization rate constant to the presence of hydrogen-bonding species.

relaxations.[30] The effect of using stretching exponential function is minimal for our results and we retain from further analysis of the stretching exponents. In our material system, the isomerization process is highly reproducible, as illustrated in Figure 1e: no changes in isomerization dynamics were observed over 250 subsequent repeat cycles (the standard deviation of the fitted time constants was 2.7%), provided that the experimental conditions (temperature, humidity) remain unchanged. Even if the azobenzene units may eventually degrade by photo-oxidation, they show potential to withstand over at least 20000 repeat cycles without significant degradation (<5% absorbance decrease).

The vapor-sensing ability of the P4VP(2PAP) complexes is based on the slight hydrophilicity of the material. Due to this, even if both P4VP and 2PAP are insoluble in water, their complex is able to adsorb a small amount of water (or other hydrogen-bonding molecules) from the environment. As shown in Figure 1f, the water vapor uptake is approximately 3.0 wt % at 90%RH, which translates to about 0.6 water molecules per 2PAP molecule for the equimolar complex. In general, more molecules will adsorb upon an increase in RH and vice versa. The shape of the adsorption isotherm depends on the chemical activity of the vapor species as well as the properties of the polymer material, and it is important for the sensing ability.

The thermal isomerization rate constant, k, shows a strong exponential dependence ($\sim e^{\lambda \cdot RH}$) on the relative humidity, RH (Figure 2a,b), and the sample-related constant, λ, is 0.0755 ± 0.0021%$^{-1}$. The rate constants at 25 °C vary from 0.01 to 3.73 s^{-1} between 2.6% and 82.7% relative humidity. The change is nearly 400-fold, and the exponential behavior suggests the difference between 0%RH and 100%RH to be 1000-fold for the equimolar complex. This yields a huge dynamic range for the isomerization-based humidity sensor. Measurements at differ-

ent temperatures reveal the Arrhenius-type ($\sim e^{-E_a/RT}$) temperature dependence (Figure 2c) of the rate constant, with apparent energy of activation, E_a, of 146 ± 7 kcal/mol. The dependence on RH is exponential at all the studied temperatures (Figure 2b). This shows that the RH and temperature dependencies are decoupled, which is an important feature from the sensing point of view. Overall, based on the results of Figure 2a−c, the time constant can be described as

$$k(T, RH) = k_0 e^{-E_a/RT} \cdot e^{\lambda \cdot RH} \quad (2)$$

where k_0 is a sample-dependent constant, E_a is the apparent energy of activation, R is the gas constant, and RH is the relative humidity at temperature T.

We believe that the RH dependence arises from the water-induced intrinsic changes in the isomerization pathway. The hypothesized mechanism is depicted in Figure 2d. The two classical routes for thermal *cis*−*trans* isomerization are inversion and rotation.[14] For an unsubstituted azobenzene molecule, inversion is favored, while for push−pull type azobenzenes, rotation is the dominating isomerization pathway. The latter has a significantly lower activation energy, resulting in shorter lifetimes of the *cis*-isomer. In 4-hydroxyazobenzenes, hydrogen-bonding to the −N═N− moiety by, for example, water or ethanol molecules shifts the azo-hydrazone equilibrium toward the hydrazone form, thus, effectively easing the rotational isomerization pathway.[31,32] This leads to a drastic decrease in the *cis*-lifetimes, that is, an increase in the thermal isomerization rate constants upon increasing RH. The lack of side reactions allows the isomerization cycles to be repeated continuously and with high accuracy, which renders hydroxyazobenzenes optimal for devising a reliable, high-performance sensor for water vapor or other hydrogen-bonding vapors.
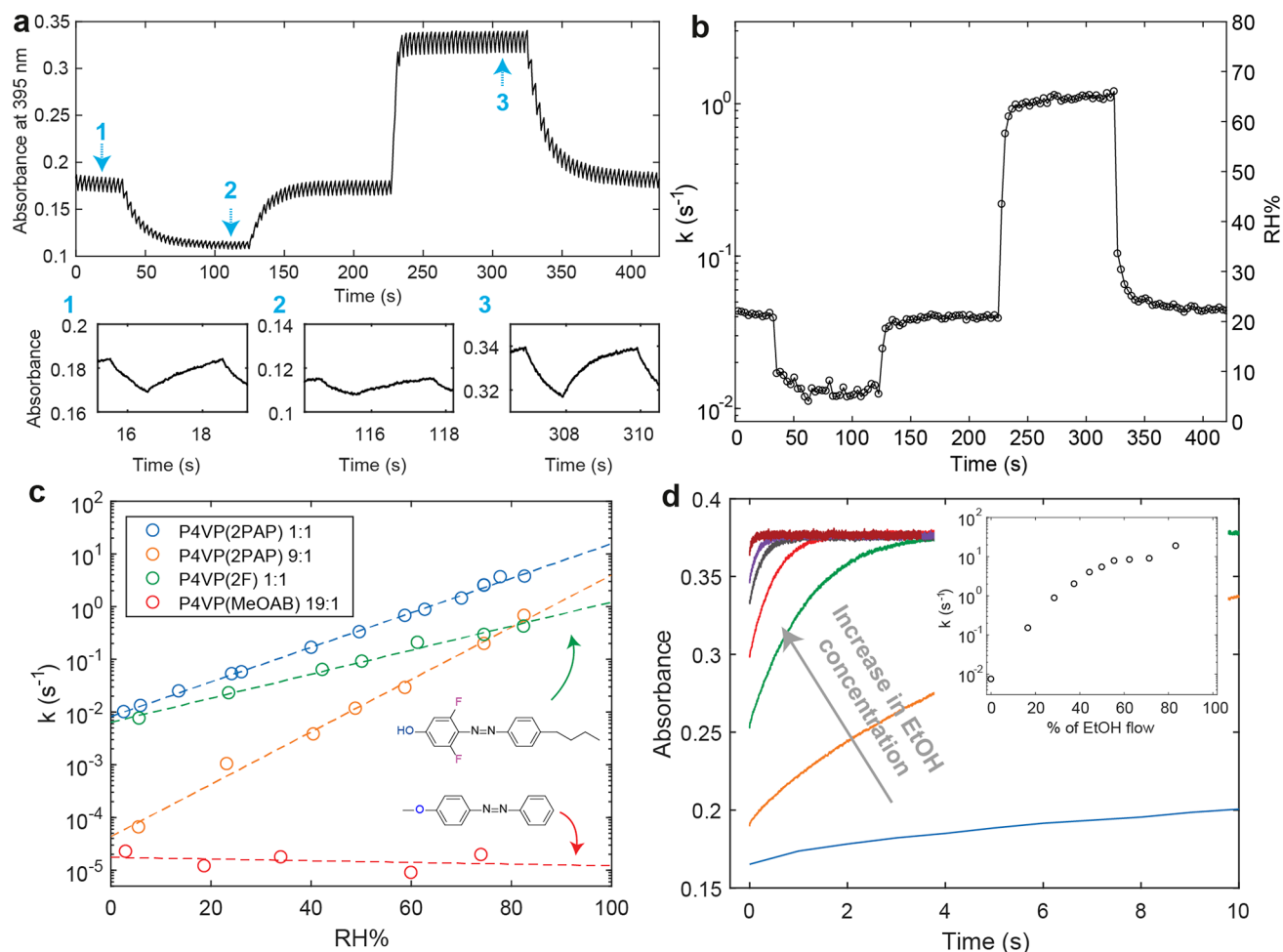
Figure 3. (a) Example of the use of the isomerization kinetics as a relative humidity sensor by pulsed UV irradiation (1 s) and following the *cis−trans* isomerization (2 s). The insets 1−3 show examples of the partial thermal relaxations (increase in absorbance) at three different RH values (∼20% RH, ∼5%RH, and ∼70%RH, respectively). (b) Rate constants extracted from the relaxations in (a) and the RH values obtained from eq 2 and data shown in Figure 2. (c) RH dependencies of rate constants for different azobenzene-containing polymer systems. (d) Sensitivity of the rate constants to the presence of ethanol. The inset shows the rate constants as a function of percentage of ethanol flow (N$_2$ bubbled through ethanol).

To demonstrate the potential of the proposed method in an actual sensing device, the sample is kept constantly in a nonequilibrium state by pulsed illumination with 365 nm light, and the kinetics of the thermal isomerization is measured for each relaxation. Upon humidity transients from ∼20%RH to low (∼5%RH) and high humidities (∼70%RH), the thermal isomerization constant changes rapidly. Based on the exponential dependence, the logarithmic scale of the rate constants is translated to linear scale of RH values (Figure 3b). A comparison to a commercial hygrometer is shown in the Supporting Information, Figure S1. Upon an increase of humidity from 20%RH to 70%RH, the response time for 90% change is 11 s and upon decrease is 15 s. The response speed is a result of the fast equilibration of the adsorption of water molecules into the polymer film, arising from the use of a thin (ca. 1 μm) active layer.

Based on our results, the hydroxyazobenzene-based vapor sensor is fast, accurate, and reliable. We note that the use of hydroxyazobenzenes is critical for it to function. This is demonstrated in Figure 3c by using 5 mol % mixtures (with respect to monomers) of 4-methoxyazobenzene (MeOAB) and P4VP. The methoxy functionality is not able to tautomerize as the hydroxy group is, and therefore, the mixture does not show any dependence on the RH. Furthermore, in higher mixing

ratios, the MeOAB phase separates from the polymer, unlike the supramolecular P4VP(2PAP) complex where the phenol−pyridine hydrogen bonding allows high azobenzene concentration to be used. Figure 3c also shows that the sensitivity of humidity detection can be optimized by changing the material composition. Using 10 mol % of 2PAP in P4VP (see Figure S2 for spectra), instead of the equimolar complexation, increases the hydrophilicity of the material system and decreases the *cis*-lifetime at dry conditions,[29] leading to a dynamic range of 5 orders of magnitude. On the other hand, when 2PAP is replaced with its *ortho*-fluorinated counterpart, 4-((4-butylphenyl)diazenyl)-3,5-difluorophenol (2F) (inset of Figure 3c; see Figure S2 for the absorption spectrum), the material becomes more hydrophobic and the hydrogen-bond-accepting ability of the *cis*-azo group weakens. Both of these decrease the RH sensitivity, as is clearly evident from Figure 3c. Overall, these results confirm the proposed mechanism, that is, that 4-hydroxyazobenzene derivatives are able to create functional sensors, the major requirement being a tautomerizable azobenzene molecule and a matrix that does not contain hydrogen-bond donors. Finally, Figure 3d demonstrates that the sensing ability is not limited to water, but the system can detect also other hydrogen-bonding vapors, as demonstrated here using ethanol. In principle, by combining different

hydroxyazobenzene molecules with distinct spectral changes into the same matrix, one can foresee the possibility of simultaneously measuring relative humidity and temperature or independently detecting several hydrogen-bonding vapors within one photoactive polymer film.

In summary, we have shown that the thermal isomerization kinetics of 4-hydroxyazobenzenes offer a robust platform for sensing hydrogen-bonding vapors. The strong dependence on the environment, that is, the high sensitivity of the device demonstrated, arises from the intrinsic changes in the isomerization pathway through tautomerization, induced by the presence of hydrogen-bond-donating molecules such as water vapor. The dependence of the thermal lifetime on relative humidity is shown to be exponential, and changes of up to 5 orders of magnitude between dry and wet conditions were observed. Importantly, the Arrhenius-type temperature dependence of thermal isomerization is decoupled from the dependence on relative humidity close to room temperature. The reproducibility of the isomerization allows using the isomerization kinetics as an optically readable vapor sensor with high accuracy. In addition to relative humidity, the sensor can detect also other hydrogen bonding vapors, as demonstrated for ethanol. The sensitivity of the device can be optimized by tuning the material composition. Importantly, the concept provides a pathway toward remote sensing of gases and vapors using fiber-optic connections and suppresses the need for device-specific calibration taken the type of the gas or vapor is known. We present here what we believe to be the first azobenzene isomerization-kinetics-based vapor sensor, yet are confident that by clever materials design, the concept can be expanded toward other types of analytes as well.

■ EXPERIMENTAL SECTION

Materials and Methods. Poly(4-vinylpyridine) (M_n = 1000 g/mol) was purchased from Polymer Source and solvents were purchased from Sigma-Aldrich and used as received. The 4-(4-Ethylphenylazo)phenol was synthesized through azo-coupling of 4-ethylaniline and phenol according to a previously published procedure,[33] and 4-methoxyazobenzene (purity > 99.0%) was purchased from Sigma-Aldrich and used as such. (*E*)-4-((4-Butylphenyl)diazenyl)-3,5-difluorophenol was synthesized through azo-coupling of 3,5-difluorophenol and diazonium salt of butyl aniline (see details from Supporting Information). Thin films were prepared by dissolving poly(4-vinylpyridine) (P4VP) and the azobenzene in question into chloroform (15 mg/mL) and mixing them to obtain the desired molar ratio. The solutions were spin coated onto glass or quartz substrates with spinning conditions chosen such that the maximum absorbance of the films would be around unity. The UV−vis absorption spectra of the thin films under dark conditions were measured using Agilent Cary 5000 spectrophotometer. The spectral change upon thermal isomerization kinetics was measured using an Ocean Optics 2000+ diode array spectrometer with a deuterium-halogen light source (DH-2000 BAL, Ocean Optics).

Thermal Isomerization Measurements. The *cis*-lifetimes were determined by following the absorbance at a single wavelength (395 or 340 nm) by using either Agilent Cary 60 spectrophotometer or a photodiode equipped with a 10 nm bandpass filter (398 nm, OD 4, Edmund Optics). A 365 nm light-emitting diode (Thorlabs) equipped with a 10 nm bandpass filter was used to induce the *trans−cis* isomerization. The intensity and duration of the illumination was controlled electronically. To avoid any unwanted isomerization, the probe beam was incident on the sample only when collecting the data and blocked otherwise. The maximum observed absorbance change at 395 nm was 70%, but the actual absorbance change is limited by the thermal rate constant (temperature, gaseous environment) and illumination intensity. Stretched exponential function (eq 1) is used

for the fitting, except in cases of partial relaxations measured upon sensing, for example, Figure 3a.

Relative Humidity Control. The isomerization measurements were done inside a temperature and humidity-controlled chamber equipped with glass windows for transmission measurements. The temperature was controlled with a resistive heating element and a Eurotherm temperature controller. The relative humidity was controlled by combining controlled flows of dry nitrogen with a flow bubbled through water. The temperature and relative humidity in the measurement chamber was measured with TESTO 635−2 hygrometer.

Dynamic Vapor Sorption. The water vapor adsorption of the equimolar complex P4VP(2PAP) was measured by dynamic vapor sorption equipment DVS ET (Surface Measurement Systems). The sorption cycle was 0−90%RH with 10% RH steps and desorption cycle employing a reverse sequence. The sample was measured as a drop-casted thin film on a thin glass substrate. The weight of the substrate was subtracted from the results.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.8b00093.

Supporting figures and synthesis details (PDF).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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