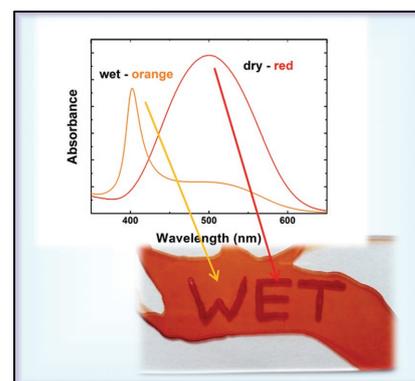


The Orange Side of Disperse Red 1: Humidity-Driven Color Switching in Supramolecular Azo-Polymer Materials Based on Reversible Dye Aggregation

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Humidity detection, and the quest for low-cost facile humidity-sensitive indicator materials is of great interest for many fields, including semi-conductor processing, food transport and storage, and pharmaceuticals. Ideal humidity-detection materials for these applications might be based on simple clear optical readout with no power supply, i.e.: a clear color change observed by the naked eye of any untrained observer, since it doesn't require any extra instrumentation or interpretation. Here, the introduction of a synthesis-free one-step procedure, based on physical mixing of easily available commercial materials, for producing a humidity memory material which can be easily painted onto a wide variety of surfaces and undergoes a remarkable color change (approximately 100 nm blue-shift of λ_{MAX}) upon exposure to various thresholds of levels of ambient humidity is reported. This strong color change, easily visible to as a red-to-orange color switch, is locked in until inspection, but can then be restored reversibly if desired, after moderate heating. By taking advantage of spontaneously-forming reversible 'soft' supramolecular bonds between a red-colored azo dye and a host polymer matrix, a reversible dye 'migration' aggregation appearing orange, and dis-aggregation back to red can be achieved, to function as the sensor.



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1. Introduction

Humidity detection, and the quest for low-cost facile humidity-sensitive indicator materials is of great industrial interest for many fields, including semiconductor processing, food transport and storage,^[1] and the pharmaceutical industry in particular,^[2] among a wide range of other humidity-sensitive products areas, from production through consumption. In recent years, great effort has been spent on developing sensitive and accurate humidity sensors,^[3-8] but of equal utility and importance from the point of the view of transporting and storing humidity-sensitive goods, is development of simple binary "moisture

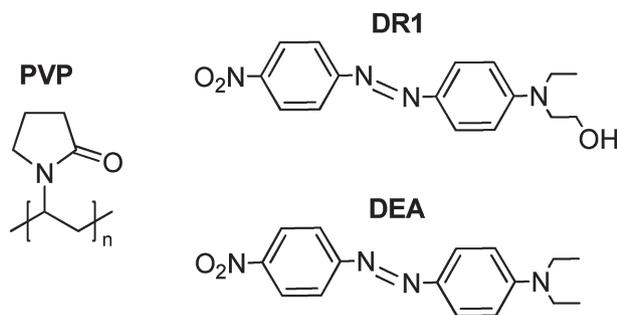
memory” packaging materials that would trigger a readout above a threshold of water content experienced, and keep the memory of this critical over-exposure to humidity in any stage of transport or storage prior to receiving the good. Conventional humidity-responsive materials are typically based on observing electrical signals,^[9] but ideal humidity-detection materials for a broad range of applications might be based on simple clear optical readout with no power supply, i.e., a clear color change observed by the naked eye of any untrained observer,^[7] since it does not require any extra instrumentation or interpretation. These ideal packaging requirements are analogous to existing optical readouts used for goods in transit that change color based on physical shock for fragile items, and temperature rise for heat-sensitive goods. Similar clear readout materials sensitive to humidity however, have proven more challenging to easily and cheaply implement. Clear visible changes have already been demonstrated by embedding photonic crystal materials in hydrogels that swell upon exposure to humidity,^[7] or the selective swelling of one block in a block co-polymer,^[4] or by borate-redox dyes,^[3] or by metal nanoparticles,^[5] whose plasmon resonance wavelength changes according to the dielectric constant of the surrounding medium. But still an achievement remains elusive of a facile “moisture memory” material based on cheap, robust, green, recyclable, and simple materials that can operate independently of readout assistance.^[10,11] Toward improved materials and methods, Vilkman and co-workers introduced an electrically readable humidity memory system based on humidity-induced changes in doping of conductive polymers,^[11] whereas Kunzelman and co-workers used a fluorescence-based approach by macrophase-separating and aggregating cyano-substituted oligo(*p*-phenylene vinylene) dyes.^[10]

Traditional covalently-bound dye-polymer materials, though long studied for applications in bioswitching,^[12] optical alignment,^[13] and photomechanical devices,^[14] are unable to achieve this reversible unbonding and aggregation, so the effect is limited to these soft-bound supramolecular polymer systems presented here. Simple guest–host mixtures lacking a supramolecular bond formation capacity are also unable to achieve this reversible unbonding and aggregation, so the effect is further confined to these soft-bound supramolecular polymer systems. Such systems offering dynamic light response have been previously reported in organogel-containing azobenzenes,^[15,16] which exhibited either solvatochromic,^[17] and photochromic,^[18] properties as well as a potential platform for humidity sensing.^[19] However, these previous material approaches still suffer from relatively complicated component preparation procedures, high cost, and complexity of the base materials, and the added processing steps required increases the cost of the final product to that prohibitive for mass production and adoption.

In this paper, we report the introduction of a synthesis-free one-step procedure, based on physical mixing of easily available commercial materials, for producing a humidity-memory material which can be easily painted onto a wide variety of surfaces and undergoes a remarkable color change (≈ 100 nm blue-shift of λ_{MAX}) upon exposure to various thresholds of levels of ambient humidity. This strong color change, easily visible to the untrained and naked eye as a red-to-orange color switch, is locked in until inspection, but can then be restored reversibly if desired, after moderate heating. By taking advantage of spontaneously forming reversible “soft” supramolecular bonds between a red-colored azo dye and a host polymer matrix, a reversible dye “migration” aggregation appearing orange, and disaggregation back to red can be achieved, to function as the sensor. Red thin film materials and regions exposed to a threshold water-content thus appear “orange,” but then the material can be switched back to its dry unaggregated “red” state by simple heating, and the humidity detection readout property can be reused multiple times.

The class of azo dye-supramolecular complexes proposed for this application has been studied previously for other uses, where it was observed that aggregation of azobenzene chromophores and the associated band shift in the absorption spectra, as well as the photoresponse of the material, can be controlled “ex situ” by varying dye doping levels of chromophore.^[20,21] This was achieved by preparing a guest–host system using Disperse Red 1 azo chromophores (DR1) (Scheme 1) embedded in a nonpolar polystyrene (PS) host with DR1 concentrations of 7 wt% (unaggregated DR1 molecules) and 40 wt% (aggregated DR1 molecules), respectively, the former exhibiting an absorption maximum at 480 nm and the latter significantly blue-shifted, at 430 nm. Upon relatively low irradiation intensity of 30 mW cm^{-2} of linearly polarized 488 nm light, a photoinduced molecular alignment against the polarization vector and a resulting associated birefringence induced in both the unaggregated and aggregated samples was essentially equal. However, for the unaggregated sample, induced birefringence values did not increase for high-intensity irradiation of 300 mW cm^{-2} , whereas for the aggregated sample, this irradiation intensity was sufficient to orient entire aggregated domains, resulting in high and very stable photoinduced birefringence. In this study, the interplay between aggregated and nonaggregated states, and resulting optical phenomena were observed between two different samples with different chromophore concentrations, and to the best of our knowledge these two color states of DR1 (red and orange), have never been demonstrated in the same material, and capable of switching reversibly between the two states.

In this study, we take advantage of the reversibility afforded by supramolecular assembly, by



Scheme 1. Chemical structures of poly(vinylpyrrolidone) (PVP), “bonding” Disperse Red 1 (DR1) azo dye, and “nonbonding” 4-diethylamino-4'-nitroazobenzene (DEA) azo dye.

introducing the DR1 molecules noncovalently to a poly(vinylpyrrolidone) (PVP) polymer backbone, which, unlike the neutral PS used in the above-mentioned study,^[20] has a carbonyl group capable of accepting a hydrogen-bond donated by the $-OH$ group of DR1 (structures depicted in Scheme 1) for noncovalent (“soft-bonding”) attachment. Previously, this supramolecular approach has proven to be a very useful method for preparing polymer-dye systems for various optical applications,^[22–26] not only because this method allows a facile and easy sample preparation without the need for complicated organic synthesis, in comparison to covalently linked polymer-dye systems, but it also allows for ready tuning over variables such as the dye/polymer ratio. Through consecutive exposures to humidity and heat, the color of this hydrogen-bonded polymer-dye system can be switched completely reversibly between clear red and orange colors, indicating dry and humidity-exposed states, over multiple cycles. For a comparison, we used the same polymer backbone combined to an otherwise identical dye to DR1 but with no $-OH$ hydrogen bonding function, 4-diethylamino-4'-nitroazobenzene (DEA, Scheme 1), as a control to assess the role of the H-bonding capacity of DR1 in how many times the material can be cycled between red and orange states. We also demonstrate as proof-of-principle that arbitrary shapes and letters can be written/printed on top of these films with the help of nonwater absorbing polymer, such as poly(styrene) acting as masking regions. These read-out texts can then be made visible by brief exposure to humid air, such as even breathing on the film, to expose only the unmasked regions, yet these revealed symbols disappear again reversibly upon briefly heating the material back to the red state. The possibility that humidity exposure leads to stable revelation of a pattern having clear contrast as compared to its background leaves little opportunity for hesitation or confusion, or whether different observers interpret different colors differently, and thus highlights a very general applicability of the design concept presented here.

2. Results and Discussion

To prepare the two materials for study, both DR1 and DEA were mixed with PVP, and before studying their use for the proposed humidity memory application, limits on the miscibility of the molecule into the PVP host polymer matrix were first established, to ascertain levels of dye loading achievable. A ready method to characterize this level is to load various increasing levels of dye into a series of PVP samples, then assess the entire sample calorimetrically via differential scanning calorimetry (DSC) until a melting of the crystalline dye alone is observed, indicating that soft-bonded loading saturation has been achieved and surpassed, and microcrystalline aggregates begin to form. As depicted in Figure S1 and Table S1 of the Supporting Information, the onset of doping levels at which melting peaks are first observed in the DSC traces when increasing the chromophore concentration in PVP, are 40% of DR1 in PVP, and 15% of DEA in PVP, respectively. A much higher doping level achievable for DR1 in PVP is a consequence of the ability of DR1 molecules to interact far more strongly with the PVP matrix due hydrogen bonding, and serves as an initial proof of the strong supramolecular interaction achievable. Additionally, increasing the chromophore/polymer ratio leads to a decrease of T_g from 162 °C of the pure PVP polymer to 116 and 112 °C, in the case of 10% doping of DR1 and DEA, respectively (see Table S1 of the Supporting Information for midpoint values for all the doping ratios tested), as expected for small molecule dilution into a polymer.^[23,27,28] Based on these DSC results, a doping ratio of 10% was chosen for comparison between the two materials, since at that concentration, both dyes are fully miscible with PVP.

Figure 1 demonstrates that when spin-coated from chloroform solutions, PVP/DR1 10% and PVP/DEA 10% yielded films red in color, with absorption maxima at 501 and 504 nm, respectively. When these films were exposed for 5 s (or less) to humid air by a nitrogen airflow at room temperature that was bubbled through water, a remarkable peak shift from ≈ 501 to 403 nm maximum in the case of PVP/DR1 10%, and 504 to 428 nm in the case of PVP/DEA 10%, was observed. There was no such color change inducible with dry nitrogen, ambient air with ambient humidity below 50%, or dry CO_2 , but only with air or nitrogen bubbled through water to achieve humidity levels above 50% RH (exhalation of one's breath onto the sample is also sufficient). The color change was also observed when the thin films were placed in an incubator at 75% RH. While there have been no systematic experiments to find a humidity threshold in this experiment, the transition was not observed below 50% RH. In principle, this threshold could be reduced at higher temperatures and the color change could occur much faster given the increase of water vapor in air at higher temperature.

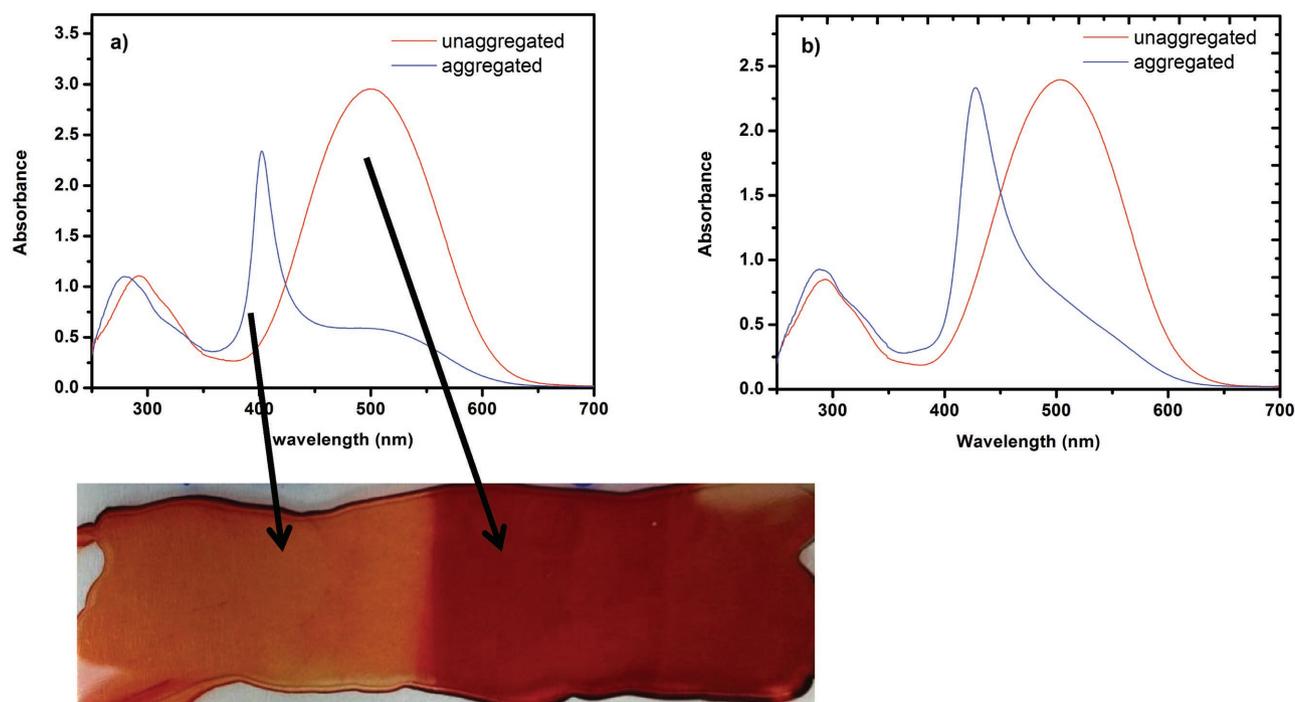


Figure 1. UV-vis absorption spectra of thin films of a) PVP/DR1 10% and b) PVP/DEA 10% in spin-coated thin films that are either dry (right half) or exposed to humid air (left half), showing the strong color change from red to orange on exposure to humid air for a few seconds.

However, no experiments were carried out at higher temperatures, as the proposed device is designed to work at room temperature. The contrast in the colors indicating dry and wet states develops rapidly on the timescale of seconds, and is strong and clear as demonstrated by a photograph of a film (inset in Figure 1), where only the left half of which was exposed to humid air. More importantly from the point of the view of any humidity memory device applications, the color change was stable, at least over the time scale of weeks, and even in room conditions of low humidity. The color change could also be localized using the narrow tip of a glass pipette used for rapid “writing,” by tracing the humid gas jet above the sample free-hand like an air-pen. By heating the samples, the peak maxima could be shifted back to 501 and to 504 nm, in PVP/DR1 10% and PVP/DEA 10%, respectively. This was accomplished by drying the films at 85 °C in an oven for a few minutes, or placing them on a hotplate of a similar temperature for a few seconds, or by brief exposure with a handheld hair dryer of a few seconds. After heating to return the red state, humid gas again could color-switch the films exactly as the first time, and this cycle repeated many times over, in the case of PVP/DR1 10%, as will be demonstrated later in detail. Film thickness can be controlled by varying spin-coating speeds. Thinner films change color more readily due to faster diffusion of water vapor, but the contrast between the two states is less clear as the color is more pale. In this experiment, the thickness was optimized to produce a mid-thickness film which

could produce a rapid transition with an obvious color change. PVP/DR1 10% was also used for methanol sensing and also yielded a color change, however this effect was not as strong as with water, possibility due to the higher solubility of DR1 in methanol.

To rationalize the observed strong and reversible humidity-induced color changes, a key difference in behavior of the polymer and two chromophores used in the presence of water needs to be considered, namely, the hydrophilicity of PVP and the hydrophobicity of DR1 and DEA. By exposing the thin films to humid air, we propose that water penetrates readily into the thin film and interacts with the PVP chains based on their H-bond donating properties. Gravimetric studies have indicated that one *n*-vinyl-2-pyrrolidone unit can accommodate up to 9.5 water molecules in the swollen state, with the carbonyl group in particular hydrogen-bonding to more than 2 at the time,^[29] and neutron reflectometry has been used to show that water can easily penetrate into thin polymer films.^[30] When the polymer is swollen by water molecules however to occupy the H-bonding sites, the energetically-favored option for the DR1 and DEA dyes, both being insoluble in water, is get replaced and to phase separate locally, resulting in the antiparallel stacking of molecular dipoles, often referred to as H-aggregation.^[31,32] The hypothesis that the orange (“wet”) state being observed is an aggregated state of DR1 or DEA molecules is further supported by Raman spectroscopy, which was used to probe the bonding environment changes occurring

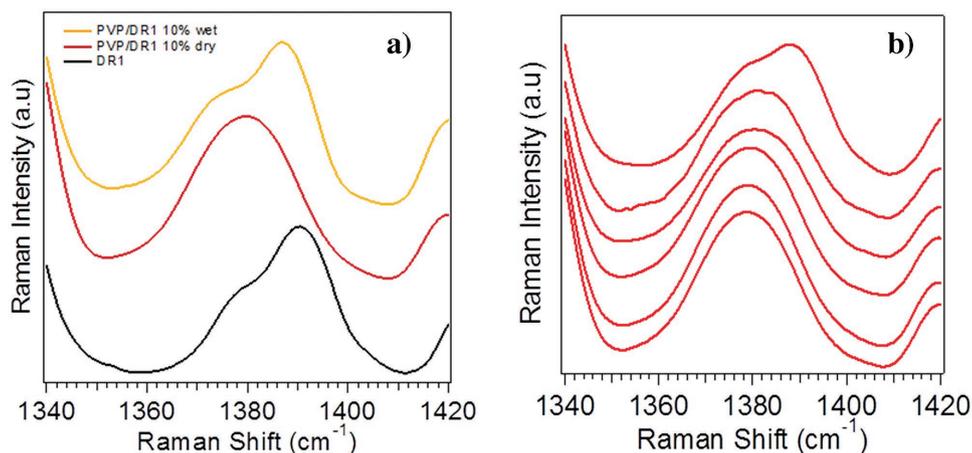


Figure 2. a) Raman spectra of DR1 (bottom trace) compared to the dry 10% DR1/PVP (middle trace) and wet 10% DR1/PVP (top trace). b) Raman spectra of a dry dye loading series of DR1 into PVP, from bottom to top in order: 10%, 20%, 30%, 40%, 50%, 75% w/w samples.

around the dye molecules. Raman spectroscopy of the dye aggregates is an especially useful technique for this study as there is little interference from water, unlike trying to probe the H-bonding environment of the polymer directly. PVP also has a very weak scattering potential and exhibits little interfering signal when mixed with DR1, regardless of dye concentration, excitation wavelength, or sample form (powdered vs drop-cast films).

Figure 2a shows a change in the asymmetric C–C stretching band of the nitro containing phenyl ring of DR1, which was found to exhibit the most sensitive shift of all bonds in the system through this exchange and aggregation process. This band is centered on 1390 cm^{-1} in the case of pure DR1,^[33] and also displays a shouldering red-shifted by about 10 cm^{-1} . The Raman spectrum of the “wet” 10% PVP/DR1 displays a similar profile. This convolution of bands in the case of pure DR1 and the wet state could indicate a mixture of aggregated and isolated dye molecules. However, the shoulder of the band becomes the main feature in the case of the dry 10% PVP/DR1 with no evidence of a shoulder at a higher wavenumber, suggesting that the majority of molecules are dispersed and isolated within the polymer matrix. Further evidence is presented in Figure 2b in which the C–C band is measured under increasing doping levels. For dye content under 40 wt%, the band is centered on 1380 cm^{-1} and matches the 10% dry PVP/DR1. At higher dye loadings however, the band broadens and a shouldering at 1390 cm^{-1} becomes prominent at 75 wt% loading. This behavior follows the same trend observed by DSC in Figure S1 of the Supporting Information and the spectra of the overloaded dyes and wet 10% PVP/DR1 exhibit the same feature.

Other bands also display modest shifts, which are consistent with the changes described above. The coupling band of the stretching phenyl-nitrogen and in-plane C–H deformation, assigned to the 1140 cm^{-1} band,^[33] is

blue shifted by about 3 cm^{-1} when comparing the dry and wet spectra of the 10% DR1/PVP and the overloaded 75% w/w. The symmetric stretching band of the nitro group also shows a similar shift, but is red shifted.

Lastly, Figure 3 depicts experimental results to demonstrate a practical utility of the H-bond forming hydroxyl group in DR1 in terms of stability and reversibility of color switching, for potential device incorporation. The same thin films of PVP/DR1 at 10% and PVP/DEA at 10% here have been moistened and dried consecutively over 7 cycles. As soon as the water in the system is largely removed, the DR1 aggregates redisperse completely and the energetically favored H-bonds between PVP and DR1 are formed again, resulting in the complete recovery of the red (molecularly dispersed) state of the DR1. This can be repeated completely reversibly, as shown in Figure 3a over 7 cycles. Figure 3b, on the other hand, demonstrates that in the PVP/DEA 10%, with every new exposure/heating cycle, more and more aggregates are not able to disaggregate completely upon drying, as the interaction between DEA and PVP is much weaker as compared to DR1, and consequentially the energetic profit of breaking aggregate interactions is much less, so this system in contrast is not observed to be reversible.

Taken together, the spectroscopic data in Figure 3 as well as Video S1 in the Supporting Information, demonstrate a strong potential of this material to be applied as a facile, cost-effective reversible humidity memory system. Arbitrary shapes, codes or texts can be easily written or printed as contrast masks on top of the ready-made spin-coated films by a writing “ink,” such as PS in tetrahydrofuran (THF), as depicted in Figure 3c–e. Due to the hydrophobic nature of the PS, these masked areas thus remain dry and thus red, when the bare film regions are exposed to humid conditions by bubbling air through water and presenting it to the entire sample (see Figure 3d). As shown by Figure 3e, these changes are then stable in

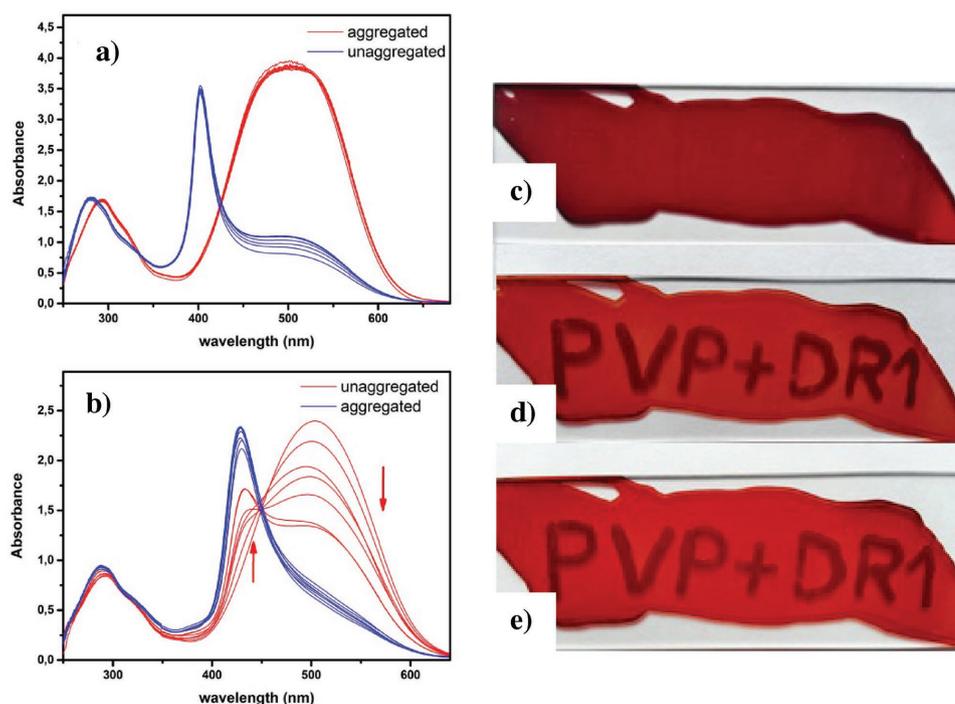


Figure 3. A demonstration of reversible readout (7 cycles of moistening and drying) of a) PVP/DR1 10% and b) PVP/DEA 10%, where PVP/DR1 (top) exhibits completely recoverable spectra over 7 cycles of drying and wetting, while the PVP/DEA (bottom) in contrast is not able to dry and cycle reversibly (back to the unaggregated state) because of the weaker dye interaction to the PVP. c–e) Capture patterning demonstrations of PVP/DR1 10% showing that hand-lettered poly(styrene) can be used as an “ink” to mask areas experiencing humid air, exposing text contrast as a readout: (c) painted but unexposed film, (d) after 5 s high humidity exposure, and (e) the same film three weeks later stored in ambient room humidity. Video S1 of the process from (c) to (d) in real time of a few seconds is available in the Supporting Information.

ambient conditions at least for a period of several weeks, depending on the film environment, and could thus be employed as a humidity detector inside packages that would indicate if the goods at any time were exposed to moisture above a critical level at any state of the transport. While some color loss is observed during the 7 cycles, the color remains stable on the timescale required for use as a humidity detector.

Our results suggest that the hygroscopic properties of PVP seem to be optimal for this application, since when tested with polymers having higher affinity to water, such as poly(acrylic acid), the initial state did not remain stable, but instead turned orange spontaneously upon storage at ambient humidity conditions. Other polymers, such as poly(4-vinylpyridine) (p4VP), poly(methyl methacrylate), and poly(dimethylaminoethyl methacrylate) were briefly investigated and none showed any color change, owing likely to their lower affinity to water. Further investigation of polymer/dye interactions might lead to a better sensitivity in the device, with multiple thresholds. The contrast between masked and nonmasked states can be tailored by tuning the film thickness, with thinner films giving higher color contrast due to better moisture penetration, and

humidity-induced changes could be then reversed completely by heating up the film briefly to 85 °C, which recovered the original color state. This could open a development pathway toward new applications in which small thin films that could indicate whether the product was exposed to certain humidity levels at any stage of the transport or storage history, and/or could be attached directly on devices and components that are especially sensitive to humidity. In addition, supramolecular complexes between different dyes and PVP might offer a cost-effective platform for externally controllable photonics materials for other applications, since, for instance, the emission and photoorientation properties of some dyes can be controlled by changing their aggregation state upon exposure to humidity.

3. Experimental Section

All chemicals were obtained either from Sigma-Aldrich Corporation or from Fisher Scientific and used as is, with the exception of the azo dyes which were recrystallized before use. ^1H NMR spectra were acquired at 300 K, on a Varian-Mercury 400 MHz spectrometer.

3.1. 4-Diethylamino-4'-Nitroazobenzene

4-Nitroaniline (1.38 mL, 10 mmol) was dissolved in a 2:1 (v/v) water:acetone mixture (150 mL) and cooled to between 0 and 5 °C in an ice bath. A solution of sodium nitrite (0.69 g, 10 mmol) and conc. HCl (1.72 mL, 20 mmol) in water (20 mL) was cooled to 0–5 °C and slowly added to the aniline solution (30 min). *N,N*-diethylaniline (1.61 mL, 10 mmol) was slowly added to the mixture with intensive stirring and left overnight. Acetone was removed using rotary evaporation and the product was extracted with diethyl ether. The diethyl ether was removed by rotary evaporation and the remaining solid was purified by column-chromatography, yielding purple red crystals (600 mg, 2 mmol, yield: 20%).^[25,26] ¹H-NMR (400 MHz, acetone-*d*₆, δ): 1.25 (t, *J* = 7.1 Hz, 6H; 2x CH₃), 3.58 (q, *J* = 7.1 Hz, 4H; 2x CH₂), 6.87–6.90 (m, 2H, Ar H), 7.88–7.90 (m, 2H, Ar H), 7.97–7.99 (m, 2H, Ar H), 8.36–8.38 ppm (m, 2H, Ar H).

3.2. Preparation of the PVP-Azobenzene Powders

The supramolecular complexes studied in this work were formed by physical mixing to enable H-bonding between PVP (*M*_w = 40 000 g mol⁻¹, *T*_g = 162 °C, Sigma-Aldrich) and the azobenzene dye Disperse Red 1 (Sigma-Aldrich, 95%). As a non-H-bonding reference we formed a similar guest–host system between PVP and the synthesized DEA to demonstrate the impact of H-bonding, attributed to the hydroxyl-group in the molecular structure of DR1. PVP and the corresponding chromophore were dissolved together in chloroform (CHCl₃, Fisher, >99.8%) in order to obtain a 2 wt% solution with the desired degree of complexation. After stirring the mixture overnight, the solvent was evaporated and the remaining supramolecular complex was dried under vacuum (85 °C).

3.3. Preparation of the Thin Film Samples

Corresponding PVP-azobenzene films were obtained by spin-casting onto clean glass slides from 5 wt% solutions, prepared similar to the complex solutions described above. The thicknesses were controlled by adjusting the spinning speed as well as the solute concentration prior to spin coating. The resultant thin films were then dried under vacuum (85 °C). Samples for Raman analysis were prepared by drop-casting a 5 wt% solution (prepared as above) onto silicon chips. The “wet” samples were prepared by storing the drop-cast films over a supersaturated solution of NaCl for 24 h and the dry samples stored under vacuum at 85 °C.

3.4. Spectroscopic Characterization

The UV/vis spectra of the thin PVP-chromophore films were measured with a Varian Cary 300 Bio Spectrophotometer. Raman spectra were obtained using a Renishaw Invia Raman microscope with a 785 nm laser line as an excitation source. The glass transition temperature (*T*_g) and melting temperature (*T*_m) were determined by DSC using a Mettler Toledo DSC1. The samples were measured over 3 cycles, heated from 25 to 180 °C, and cooled over the same temperature range, using a heating rate of 10 °C min⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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