Photo-Induced Assembly of Nanostructures Triggered by Short-Lived Proton Transfers in the Excited-State

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S *Supporting Information*

ABSTRACT: Light stimulation was used to trigger the assembly of nanostructures by directly powering changes at the supramolecular level without incurring net chemical changes at the molecular level. Polyethylene imine, a polybase, was mixed in aqueous solution with sodium 1-naphthol-4-sulfonate, an aromatic alcohol, which, in the electronic excited-state, undergoes a short-lived increase in acidity. Excited-state proton transfers between these components were induced by photoexcitation, which led to the formation of hydrogen bonds in the ground-state. Ionic forces, $\pi-\pi$ stacking, and hydrophobic effect provided further stabilization. The photoinduced formation of nanosized aggregates was detected by dynamic light scattering and atomic force microscopy. Absorption and emission spectroscopy were used to rule out photochemical reactions and elucidate the supramolecular arrangement.

The direct transformation of energy from the electronic excited-state of molecules into supramolecular ground-state reconfigurations without involving net chemical changes opens new perspectives for an energetically optimized use of light in stimuli-responsive supramolecular chemistry. In general, self-assembly bears great potential for the formation of versatile, switchable, and functional nanostructures.[1−8] Of particular interest is a structural or functional responsivity to light, for example, in the area of solar energy conversion or photodynamic therapy, and it is desirable to explore novel concepts toward light triggerable self-assembly. This, in most cases, has been explored using functional groups, which undergo photochemical transformations, including the cis−trans isomerization of azo functionalities,[9−18] ring openings,[19,20] charge generation,[21,22] or the release of ions.[23] In an exact consideration, light energy does not directly power changes at the supramolecular level but rather transformations at the molecular level, which themselves trigger supramolecular reconfigurations in the ground-state. As the chemical identity changes, complementary photochemical transformations are necessary for reversibility. Besides these systems, the light-triggered formation of assemblies stabilized in the ground-state has also been attained without net chemical transformations: supramolecular stacked columns result from photoinduced changes in the electronic charge distribution of triarylamines.[24,25]

Herein, we demonstrate a concept to trigger ground-state hydrogen bonding through excited-state proton transfer. Several aromatic alcohols known as photoacids show a short-lived increase in the acidity of the hydroxyl proton in the electronic excited-state.[26−28] The photoresponsiveness relies on the structural similarity of hydrogen bonding and acid−base proton transfers. A sudden and short-lived change in acidity caused by photoexcitation of a photoacid, in the presence of a polybase, can trigger the formation of H-bonded nanostructures. These are then stabilized in the ground-state by additional types of noncovalent binding that come into effect. The system is based on electrostatic self-assembly, a versatile strategy toward discrete nanosized assemblies relying on the interplay of orthogonal interactions.[9,29−31] Triggering hydrogen bonding is a promising tool in supramolecular chemistry. Among noncovalent interactions, H-bonding presents a particular degree of structural specificity, directionality, and a number of possible counterparts. This allows, for instance, the specific association of base pairs in DNA.[32,33] Examples of synthetic systems based on H-bonding include self-assembled colloids,[34] pore-forming macromolecules,[35] or supramolecular polymers.[36−41] pH responsiveness and self-healing properties can derive from the reversibility of hydrogen bonds.[42−46]

Sodium 1-naphthol-4-sulfonate (NS) and linear polyethylene imine (LPEI; $M_n \approx 423$ g mol^{-1}) were used as building blocks of the light-triggerable system (Scheme 1). Two types of non-

Scheme 1. Building Blocks for Light-Triggerable Supramolecular Assembly: Linear Polyethylene Imine (LPEI) and Sodium 1-Naphthol-4-sulfonate (NS)
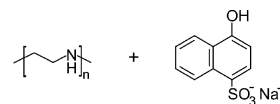
covalent bonds can be formed between NS and LPEI: an ionic bond between the sulfate group and a protonated amine, and a hydrogen bond between the hydroxyl group and a non-protonated amine. The hydroxyl group of NS has well-established photoacidic properties, with the ground-state acidity constant $pK(S_0) = 8.27$, strongly decreasing to a value of $pK(S_1) = -0.1$ in the electronic excited-state.[47]

LPEI and NS were mixed in aqueous solution with final concentrations c(N atoms, LPEI) = 2 mM and c(NS) = 1 mM. This 2:1 ratio represents a stoichiometric balance of the total number of anchoring groups from each component. A basic pH of 8.4 was measured, which can be attributed to the protonation of amine groups through water dissociation, thus rendering LPEI a polyelectrolyte character. For the photoirradiation experiment, a sample of the solution was placed in a quartz cell under oxygen-free conditions. The rest of the original solution was kept under light isolation and oxygen-free conditions for comparative measurements. Figure 1 shows dynamic light scattering (DLS)
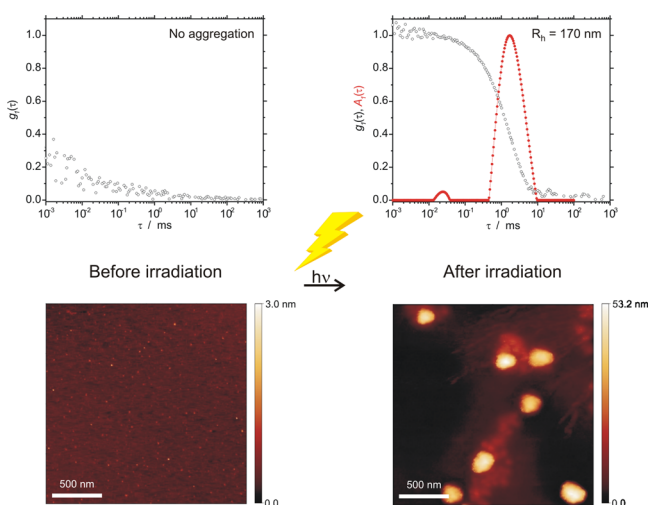

Figure 1. Sample solution of LPEI/NS before (left) and after (right) UV irradiation (10s). Top: DLS; electric field autocorrelation function $g_1(\tau)$ and distribution of relaxation times $A(\tau)$. Bottom: AFM height images. (c(N atoms, LPEI) = 2 mM, c(NS) = 1 mM).

and atomic force microscopy (AFM) results for the sample before (left) and after photoirradiation (right). Originally, the sample showed no correlation in DLS (Figure 1, top left), which is indicative of a homogeneous solution without nanoscale aggregates. In contrast, an intensity autocorrelation function is detectable on the same sample already after a period as short as 10 s of UV photoirradiation (Figure 1, top right).[49] DLS yields an average hydrodynamic radius of R_h = 170 nm. The sample also shows an increase in scattering intensity of 250%, and angular-dependent DLS confirms translational particle motion (diffusion). These results can be attributed to light-triggered aggregation. This was confirmed by AFM, which shows that the photoirradiated sample consists of globular aggregates with diameters of 230 ± 100 nm (Figure 1, bottom right). The AFM result is in good agreement with the DLS result.[50] Moreover, the AFM image of the original solution (Figure 1, bottom left) showed only minor particles with sizes <25 nm, which were not detected by DLS and hence can be attributed to agglomeration of the material as a result of the drying process on the wafer surface during AFM sample preparation. Further DLS analysis shows that the aggregates are stable for several weeks at least and that during this time no aggregation took place in the NS/LPEI original solution. A closer inspection of the globular aggregates found in the photoirradiated sample revealed intricate structural features. As seen in the AFM phase image (Figure 2), the architecture of the aggregates appears to result from the rolling up of elongated substructures. This may be understood in terms of the curvature that evolves when perpendicular levering forces
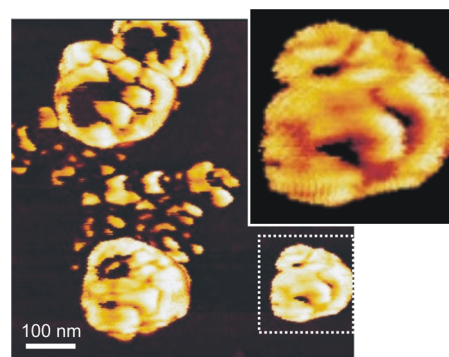

Figure 2. AFM phase image of the photoactivated LPEI/NS sample.

act on extended structures. The NS molecules that associate with the polymeric chains through ionic and hydrogen bonds can simultaneously form stacks via π–π interactions. Since the amine–amine distance along the polymer chain and the π–π distance of the stack differ, bending forces emerge.

Changes in the UV absorption of the sample were detected along the photoaggregation process (Figure 3a). Slight variations in the intensity of the absorption bands occurred directly after photoirradiation, when aggregates could already be detected by DLS. Interestingly, further variations proceeded in the same direction in the following days, while the photoirradiated sample rested under light isolation. No alterations could be detected over this period of time in the NS/LPEI original solution. Thus, photoirradiation can be identified as trigger for the spectral variations. These changes are analogous to those observed in solutions of NS only at different pH (Figure 3b). The dependence of NS spectra on pH has previously been interpreted as the presence of two balancing states: the NS *naphthol form* and its deprotonated *naphtholate* counterpart.[51] The isosbestic points observed at λ = 238 nm, λ = 262 nm, and λ = 309 nm correspond to wavelengths equally absorbed by either NS form. Thus, photoexcitation triggers a process of progressive enrichment of the NS *naphthol form* in the ground-state over the *naphtholate form.* The isosbestic points in the photoirradiated sample demonstrate the constant NS concentration, ruling out photo-degradation.

Photoluminescence spectroscopy provided complementing information (Figure 4). Previous studies have identified that the NSA *naphthol* and *naphtholate* forms have emission bands at $\lambda \approx$ 369 nm and $\lambda \approx$ 427 nm, respectively (see Supporting Information). Since the emission of naphthol derivatives is effectively quenched by hydronium ions,[47] portions of the NS/LPEI original solution and the photoirradiated sample were drop-cast onto quartz substrates. For quantitative comparison, spectra were normalized at the emission band of the NS *naphthol* form. Evidently, in the excited-state (during the photoluminescence experiment), the relative content of the deprotonated *naphtholate* form is comparable in the dried NS/LPEI mixture and the NS. The possibility to observe the *naphtholate* form in the excited-state can be understood in terms of the hydrogen bonds between hydroxyl groups forming in the pure *naphthol* crystal.[48] In contrast, a higher relative content of the *naphtholate* form in the excited-state is observed for the prephotoirradiated NS/LPEI sample. Hence, upon photo-irradiation of the NS/LPEI solution, NS hydroxyl groups are rearranged into an environment that comparatively favors excited-state proton transfers, that is, stand in the proximity of a base. However, absorption spectra show that after photo-
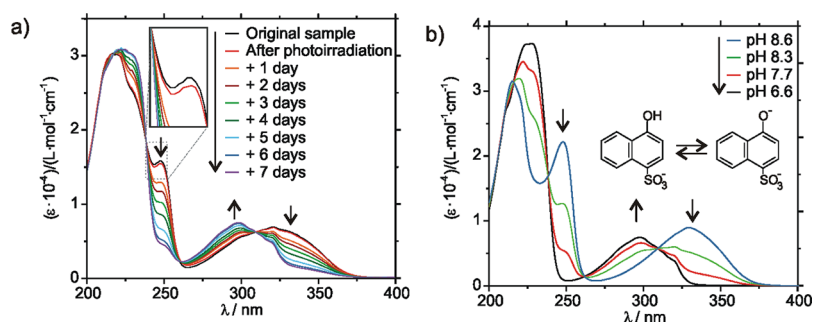
Figure 3. UV absorption spectroscopy: (a) LPEI/NS solution before and after 10 s of photoirradiation and after standing in the dark; (b) NS (without polymer) at different pH values.
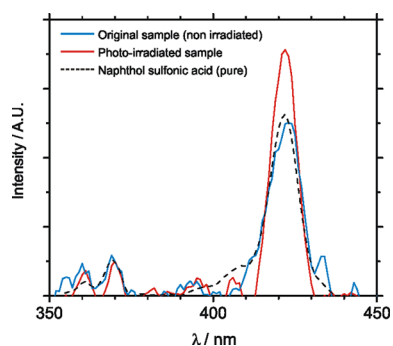

Figure 4. Photoluminescence spectra (excitation $\lambda = 270$ nm) of dropcasted portions of the NS/LPEI original solution, the photoirradiated sample, and a NS solution.

irradiation of the NS/LPEI sample, the proportion of NS molecules in the *naphtholate* form decreases. Considering that absorption and photoluminescence are indicative of the relative contents of the NS *naphthol* and *naphtholate* forms in the ground- and the excited-states, respectively, the spectral changes triggered by irradiation must be caused by supramolecular rearrangements, which result in the formation of H−N bridges.

In combination, the following possible mechanism of structure formation (Scheme 2) is in agreement with the experimental evidence for a light-induced assembly of building blocks (A) into a supramolecular nanostructure (F). Initially, LPEI chains in the solution are partially protonated (A). The addition of NS "counterions" gives rise to interactions between the cationic macromolecules and the oppositely charged ionic groups of the NS (B). Upon irradiation, the absorption of a photon by an NS molecule takes place (C), which triggers a supramolecular rearrangement process to form an interconnected structure (D). In the excited-state, the aromatic hydroxyl proton is highly acidic and interacts with an amine group in its vicinity, displacing the solvating water molecules. After decaying to the ground-state, the interaction of the hydroxyl group and the amine N atom decays from a strong ionic force to a hydrogen bridge (E). The desolvation of the amine groups and an increased association of NS results in an hydrophobization of the polymeric chains, so the building blocks of the system come into closer proximity with one another, and rearrangements driven by a combination of hydrophobic, $\pi-\pi$, and electrostatic interactions take place. This also explains the comparatively slow changes that proceed in the dark after photoactivation, as detected by UV spectroscopy (F). The stabilization of the supramolecular structure may be understood in terms of the cooperativity of the hydrogen bonds and the hydrophobic interactions, in a similar manner as observed for the stabilization of base pairs in DNA strands.

Scheme 2. Schematic Representation of a Possible Mechanism for the Photoinduced Assembly of NS and LPEI
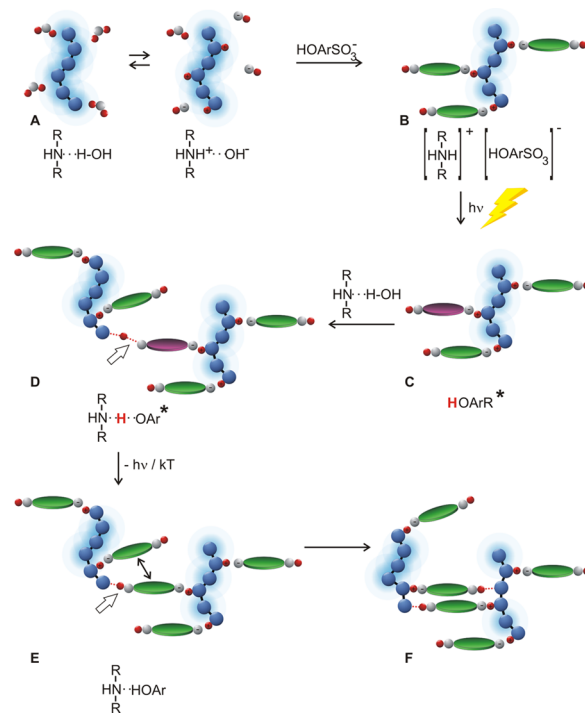
Finally, it was tested whether the phenomenon holds for varying systems. Photoinduced assembly of a photoacid with a different backbone, 8-hydroxypyrene-1,3,6-trisulfonate (HPT), and LPEI was investigated (data see Supporting Information). Results again reveal supramolecular rearrangements, which lead to a facilitated quenching process. Hence, photoinduced assembly formation through short-lived proton transfers in the excited-state can be based on different aromatic alcohols. Moreover, the polybase component has been varied. NS with a branched PEI of higher molar mass again demonstrates the effect, even if to a smaller extent. Thus, the concept described herein is of general nature and builds the basis for a variety of irradiation triggerable supramolecular structures.

In conclusion, the possibility to trigger hydrogen bonding with light stimuli has been established. Results indicate that inducing intermolecular excited-state proton transfers, despite being short-lived, can initiate supramolecular rearrangements, which lead to the formation of N−H bridges and thereby nanoscale structures in the ground-state. This represents a strategy toward light-responsive supramolecular chemistry in which changes are directly powered by short-lived photophysical process without

the need for photochemical transformations. This opens the possibility for the development of multiresponsive systems, in which different components can be selectively stimulated using light of different wavelengths.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and additional DLS, AFM, and photoluminescence. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b01357.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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