**Phototriggered Supramolecular Assembly**

Anurag Mukherjee and Suhrit Ghosh*

**ABSTRACT:** Most of the supramolecular structures lack accuracy at the macroscopic scale because of their spontaneous uncontrolled self-assembly. Although significant progress has been made in understanding the pros and cons of various directional noncovalent interactions and their specific molecular recognition ability, it is only in the recent past that the focus has been shifted toward controlling the dimension, dispersity, and other macroscopic properties of supramolecular assemblies. In this context, recent examples encompass various external stimuli to gain the structural precision in supramolecular assembly, among which light-triggered supramolecular assembly has gained significant interest as it is reagent free and endows the possibility of the controlled synthesis of supramolecular assemblies via manipulation of the light energy, irradiation time, or spatial control. This mini-review highlights representative recent examples of phototriggered supramolecular assemblies (from the monomer or another type of assembly) by removal of a photolabile protecting group, photosensitization, or other methods of photoactivation of a dormant building block.

**INTRODUCTION**

In the past three decades, supramolecular chemistry has traversed infancy and has enabled the synthesis of diverse molecular assemblies with well-defined internal order from wide-ranging π-systems, peptides, or other building blocks. However, counterintuitively, a majority of these examples lack structural precision at the macroscopic scale owing to the uncontrolled spontaneous assembly from the unimer when dispersed in a suitable medium. In the recent past, living supramolecular polymerization has emerged as an important tool which blocks the spontaneous assembly by trapping the active monomer in an off-pathway aggregate or an inactive conformation. Subsequent addition of a seed or specific molecular entity initiates a controlled supramolecular polymerization of such a metastable off-pathway aggregate/monomeric state. Whereas this is considered to be a paradigm shift in the field, its success relies on the formation of a far from equilibrium kinetic product which limits the generalized applicability to structurally diverse building blocks. In this context a pro-monomer approach could be attractive in which the building block as such exhibits a stable monomeric state but undergoes the supramolecular assembly only in the presence of an external stimuli such as pH, enzyme, or light. Among these, light-sensitive pro-monomers have certain advantages because their supramolecular assemblies can be triggered under a reagent-free condition; they may offer a scope for location-specific supramolecular assembly, and the extent of conversion can be controlled by adjusting the light energy/irradiation time. Although a large number of small molecule and polymeric self-assembled systems have been reported to show light-responsive disassembly, relatively less examples are known on light-triggered supramolecular assembly. In this mini-review, we highlight the recent progress in the field by collating representative examples on phototriggered supramolecular assemblies. As will be evident from the discussion in the following sections, such externally regulated supramolecular assembly may enable topochemical supramolecular synthesis, which may provide new opportunities for applications in sensing, making patterned surfaces or biomedicine. Early examples on this topic have been reviewed elsewhere and thus are excluded from this mini-review. Also, the vast literature of photoresponsive supramolecular systems has not been covered in this short review as they are out of the scope in context of the topic of this mini-review.

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This approach allows the activation of a pro-monomer by light irradiation and controlled self-assembly as the spatial, temporal, and concentration variables can be manipulated as per requirements. A supramolecular synthon can be converted to a pro-monomer via blocking the functional group,
responsible for the assembly process, with a photoremoveable protecting group so that light irradiation at a particular wavelength leads to the demasking followed by supramolecular assembly. Prominent examples on photolabile protecting groups (Figure 1) are nitrobenzyls, benzoyl benzoate esters, benzoins, phenacyls, coumaryls, aryl methyl esters anthraquinone-2-ylmethoxy carbonyl (agmoc), and thiopixyl moieties.11

Among them the ortho-nitrobenzyl (ONB) group has been widely used as a protecting group for deactivating the H-bonding ability of different functional groups such as amine, carboxylic acid, alcohol, or nitrile and generating the active monomer by photoirradiation ($\lambda = 254$ or 350 nm), leading to a gradual evolution of the supramolecular assembly in a controlled fashion. Stupp and co-workers explored the self-assembly of a peptide-based amphiphilic system (1, Figure 2) equipped with the photoresponsive ONB unit.12 Supramolecular assembly of the peptide was found to be guided by the formation of a $\beta$-sheet through hydrogen bonding and hydrophobic interactions among the amphiphilic chains, leading to the formation of complex supramolecular quadruple helical fibers having uniform width and helical pitch of $33 \pm 2$ and $92 \pm 4$ nm, respectively. Close inspection revealed that the quadrupole helices comprised two smaller double helical fibers, which were further composed of two nonhelical, cylindrical fibrils. However, irradiating the aqueous solution of 1 with UV light removed the ONB functionality and reduced the quadruple helices into uncomplicated cylindrical fibers with the diameter of 11 nm. They hypothesized that the bulky ONB group prevented the well-defined intramolecular packing and compelled interactions among molecules in the neighboring nano-fibers, which helped in the formation of higher-order supramolecular architectures. Photoremoval of the bulky ONB group initiated ordered packing among this peptide-based supramolecular building block into elementary nonhelical fibers.12

Meijer and co-workers reported an ABC triblock copolymer containing pendant benzene-1,3,5-tricarboxamide (BTA) with ONB-protected amide moieties in one of the blocks (Figure

Figure 1. Structures of common photolabile protecting groups.

Figure 2. (a) Reaction scheme depiction of phototriggered conversion from peptide 1 to peptide 2; TEM images of (b) complex quadruple helix produced by 1 and (c) elementary nonhelical fibers produced by 2. Adapted from ref 12. Copyright 2008 American Chemical Society.
The native polymer remained as a unimer as the bulky ONB groups prevented self-assembly of the BTA. Photolysed removal of the ONB groups resulted in stepwise intrachain folding and formation of single chain nanoparticles driven by helical stacks stabilized by three-fold hydrogen bonding among the BTA units. These chiral nanoparticles showed significantly enhanced stability compared to the supramolecular polymers of the C₃-symmetric BTA derivatives.

Our group recently reported photoinitiated supramolecular assembly of a naphthalene diimide (NDI) building block in which the amide group was protected by the ONB moiety (5, Figure 4). The pro-monomer 5 remained in the monomeric state in a dilute solution in methyl cyclohexane (MCH) as the blocked amide group could not participate in H-bonding. Removal of the ONB group by UV light irradiation (\( \lambda = 254 \) nm) produced the active monomer 6 with a free amide group, which drove the supramolecular assembly via self-complementary H-bonding. Interestingly, it was noticed that the morphology of the end product by phototriggered supramolecular assembly was quite different than spontaneous supramolecular assembly of 6. Whereas the phototriggered supramolecular assembly produced spherulite-like morphology, the active monomer on its own showed entangled fibrillar morphology with uncontrolled growth. It was rationalized by a distinct mechanism (Figure 4) of the phototriggered supramolecular assembly. At the early stage of photoirradiation, when only a small amount of the free amide was produced, they encountered a large excess of the ONB-protected amide, which still could participate in the H-bonding using the carbonyl oxygen atom of the protected amide group which was responsible for shaping the nuclei/seed which could not coalesce as they could only grow from one end while the other growth direction was blocked by the ONB group. With subsequent photoproduction of free amide, in situ generated seeds acted as the initiating site and were propagated by a chain-growth mechanism.

General applicability of the strategy was tested by exploring phototriggered supramolecular assembly of another NDI-based building block (7, Figure 5) which contains an ONB-protected carboxylic acid. Like the previous example (5, Figure 4), monomer 7 also did not exhibit supramolecular assembly in MCH due to lack of H-bonding between the ONB-protected –COOH groups. Photoirradiation yielded the active monomer (8) with a free COOH moiety, which facilitated face-to-face stacking of NDI chromophores driven by hydrogen bonding in MCH. Phototriggered supramolecular assembly produced an ultrathin (height \( \approx 2.0 \) nm) two-dimensional sheet, which differed from the fibers produced by the spontaneous assembly of the unprotected monomer (8), which was attributed to the different supramolecular assembly pathway. In the case of spontaneous assembly of 8, primarily, the catemer-type extended H-bonding produced a β-aggregate, whereas in case of the phototriggered supramolecular assembly, face-to-face π-stacking was evident (Figure 5).

Qu and co-workers recently reported photoinduced supramolecular polymerization based on host–guest interaction involving an AB-type heteroditopic linear monomer (9) containing dibenzo-24-crown-8 macrocycle and dibenzylammonium together (Figure 6). The terminal dibenzylammonium site was anchored with a photolabile bulky coumarin group which prevented host–guest interaction with the crown ether and thus restricted the supramolecular polymerization. Exposure to UV irradiation at 320 nm removed the bulky coumarin group, which led to spontaneous supramolecular assembly via host–guest recognition. At an increased concentration of the monomer, gel formation could be observed consisting of fibrillar morphology.

### SUPRAMOLECULAR ASSEMBLY BY PHOTOISOMERIZATION

Photoisomerization involves reversible or irreversible transformation between geometric and structural isomers of a same compound induced by photoexcitation. The isomerization process generally involves a characteristic color change, and thus different absorption spectra can be observed for the two isomers. Among the photoisomerizable groups, azobenzenes, stilbenes, norbornadienes, spiropyrans, and aryloxoprazoles are the most common (Figure 7). Change in geometry and/or polarity of the molecule during photoisomerization has been utilized to regulate supramolecular assembly of various building blocks. While this literature is vast and reviewed elsewhere, in this mini-review, we only have included recent examples on photoisomerization induced supramolecular assembly or modulation of supramolecular assembly. Examples

![Figure 3](image3.png)  
**Figure 3.** (a) Structure of BTA-containing triblock copolymer before and after UV irradiation. (b) Schematic presentation showing formation of single chain polymeric nanoparticles (SCPNs). Adapted with permission from ref 13. Copyright 2011 Wiley-VCH.

![Figure 4](image4.png)  
**Figure 4.** (a) Conversion of the ONB-containing pro-monomer into NDI-based active supramolecular building block. (b) Proposed model for the phototriggered supramolecular polymerization. Adapted with permission from ref 14. Copyright 2016 Wiley-VCH.
Lin and co-workers reported an amphiphilic Janus-like asymmetric molecular double brush (MDB) copolymer (11, Figure 8) with hydrophilic PEO and hydrophobic oxyazobenzene chains grafted to a polyacrylate backbone. In H$_2$O–THF medium, it initially self-assembled into spindle-like aggregates driven by \( \pi \)-stacking induced ordered alignment of the azobenzene-containing brushes. However, irradiation at 365 nm invoked reversible photoisomerization of the trans-azobenzene into cis-form, which resulted in a morphology transition into toroid-shaped nano-objects.

Stang, Huang and co-workers reported a bidentate dipyridyl donor ligand with a central Z-configured stiff-stilbene unit (12, Figure 9), which self-assembled in the presence of two 180° di-Pr(II) acceptors, leading to the formation of a discrete organoplatinum(II) metallacycle (Figure 9). UV irradiation at 387 nm caused a cis- to trans-isomerization that opened the cyclic complex and triggered the formation of an open chain extended metallo-supramolecular polymer, which on disassembly have been excluded from this article as they are out of the scope.

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was assisted by the conformational switching of the dipyridyl ligand from $Z$ (0°) to $E$ (180°) form.

Yagai and co-workers reported the synthesis of supramolecular nanofibers with circularly and helically folded structures based on photoisomerizable azobenzene monomer rosettes (Figure 10). These two supramolecular motifs were found to have distinct topology. Exposing the mixture of the two types of nanofibers to UV irradiation ($\lambda = 365$ nm) selectively photoisomerized the trans-azobenzene units to cis-form, and the helically folded fibers deformed into extended structures while the circular structures remained unaltered.

Living supramolecular polymerization of a photoisomerizable amide-containing azobenzene derivative (16, Figure 11) has been recently reported by Sugiyasu, Takeuchi, and co-workers. Light irradiation at 351 nm acted as the trigger to regulate the activity of such monomer in a controlled fashion. The trans-form of 16 acted as the active monomer that showed spontaneous $J$-aggregation via a cooperative mechanism to form 1-D nanofiber. In contrast, the cis-form served as a dormant monomer which could be transformed to the active monomer by light irradiation. When such photoisomerization was conducted in the presence of a seed of the preformed supramolecular polymer, controlled/living supramolecular polymerization was achieved.
assembly could be realized by a chain growth mechanism. The length of the resulting supramolecular polymer could be regulated by controlling the duration of UV light irradiation.25

■ OTHER EXAMPLES

Apart from the photochemical approaches discussed earlier, emerging reports indicate other possibilities to attain elegant supramolecular materials via phototriggered assembly. A C\textsubscript{3}-symmetrical triarylamine building block (17, Figure 12) was reported by Giuseppone and co-workers\textsuperscript{26} which underwent intermolecular assembly into nanowires by visible light irradiation. The supramolecular nanowires could stabilize the initially formed radicals via an extended electronic delocalization throughout the triarylamine stacks and exhibited large conductivity values (>5 × 10\textsuperscript{3} S m\textsuperscript{-1}) along with very low interface resistance (<2 × 10\textsuperscript{-4} Ω m\textsuperscript{-1}). The highly conductive nanowires were even able to cross the gap between the two electrodes and established a conductive pathway.

Gröhn and co-workers observed excited-state proton transfer between polyethylene amine and 1-naphthol-4-sulfonate in the solution phase via photoexcitation (Figure 13). The short-lived photophysical process could initiate supramolecular rearrangements that directed N–H bridge formation. While photodimerization could be successfully probed by several spectroscopic techniques (UV–vis, \textsuperscript{1}H NMR, and HRMS), and the reversibility of the supramolecular polymerization was explored via a thermal retro-reaction. Selective light-induced photoreactions, such as photoinduced cycloadditions, are greatly influenced by the spatial arrangements of the substrates. In this context, programmed supramolecular self-assembly can prove to be useful as it provides a platform with suitable topology for the photoactive substrates for controlled photochemical reactions. Fernández and co-workers demonstrated control over the photochemical behavior of substituted cyanostilbenes by solvent-dependent supramolecular assembly.\textsuperscript{29} A cyanostilbene-based bola-amphiphile (22, Figure 15) remained molecularly dissolved in organic solvents (DCM, THF, etc.), and light irradiation (365 and 465 nm) triggered a highly reversible and quantitative E/Z photoisomerization. However, introduction of aqueous medium prompted the formation of emissive J-type supramolecular polymers that underwent a [2 + 2] photocycloaddition in the

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**Figure 12.** (a) Chemical structure of C\textsubscript{3}-symmetrical triaryl amine building block that forms phototriggered nanowires. (b) Self-construction of nanowires of in a nanotrench. Adapted with permission from ref 26. Copyright 2012 Springer Nature.

**Figure 13.** Schematic representation of for the photoinduced assembly formation involving proton transfer. Adapted from ref 27. Copyright 2015 American Chemical Society.

**Figure 14.** H-bonding regulated supramolecular assembly of 20 via anthracene photodimerization. Adapted with permission from ref 28. Copyright 2003 Royal Society of Chemistry.
presence of the visible light via a precise topochemical arrangement.  

Ajayaghosh and co-workers explored the Diels−Alder photocycloaddition of 9-phenylethynylanthracene (23, Figure 16) that resulted in either [4 + 2] or [4 + 4] cycloaddition products in the solution phase. The selectivity toward a specific photoproduct could be controlled under restricted environment via regio- and stereospecific reaction. Suitable confinement could be obtained via H-bonding in the gel state of the molecule that selectively led to [4 + 2] cycloaddition product (24), and a device having white electroluminescence property was also fabricated. 

### SUMMARY AND OUTLOOK

In this mini-review, we presented an overview on the recent development in the field of phototriggered supramolecular assembly, producing well-defined nanostructures by external regulation. In one type of the system, classical photolabile protecting groups for amide, carboxylic acid, or other functional groups enable the synthesis of a pro-monomer, incapable of self-complementary H-bonding, and thus the onset of the supramolecular assembly can be regulated by light trigger. In the other set of systems, photoisomerization of suitably designed building blocks leads to the formation of new supramolecular structures which are often reversible in nature. Few discrete examples have also been covered that involve self-assembly via photoinitiated radical generation, proton transfer, or photodimerization. Supramolecular assembly by this phototriggered approach has been proven to be advantageous to retard the spontaneous assembly and thereby guiding the controlled supramolecular assembly under thermodynamic control. Although there are some arguments on the fate of the photocleaved byproducts or structural deterioration during photoirradiation, the concept offers a broad scope for designing new stimuli-responsive materials by suitable monomer design. Until now, in most of the examples, UV light has been used, which offers limited scope for exploring applications in the biological domain. In this context, new systems which are sensitive to the IR could bring new opportunities in the field of stimuli-responsive supramolecular biomaterials.  

For example, it has been reported that enzyme-triggered intracellular supramolecular assembly can induce cellular apoptosis, help in preservation of cell membrane, and regulate other important biological events. Such possibilities can be explored with suitably designed phototriggered self-assembly systems with the advantage of target-specific supramolecular assembly by localized light irradiation.

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