Self-Assembly

DOI: 10.1002/anie.201001833

The Hierarchical Self-Assembly of Charge Nanocarriers: A Highly Cooperative Process Promoted by Visible Light**

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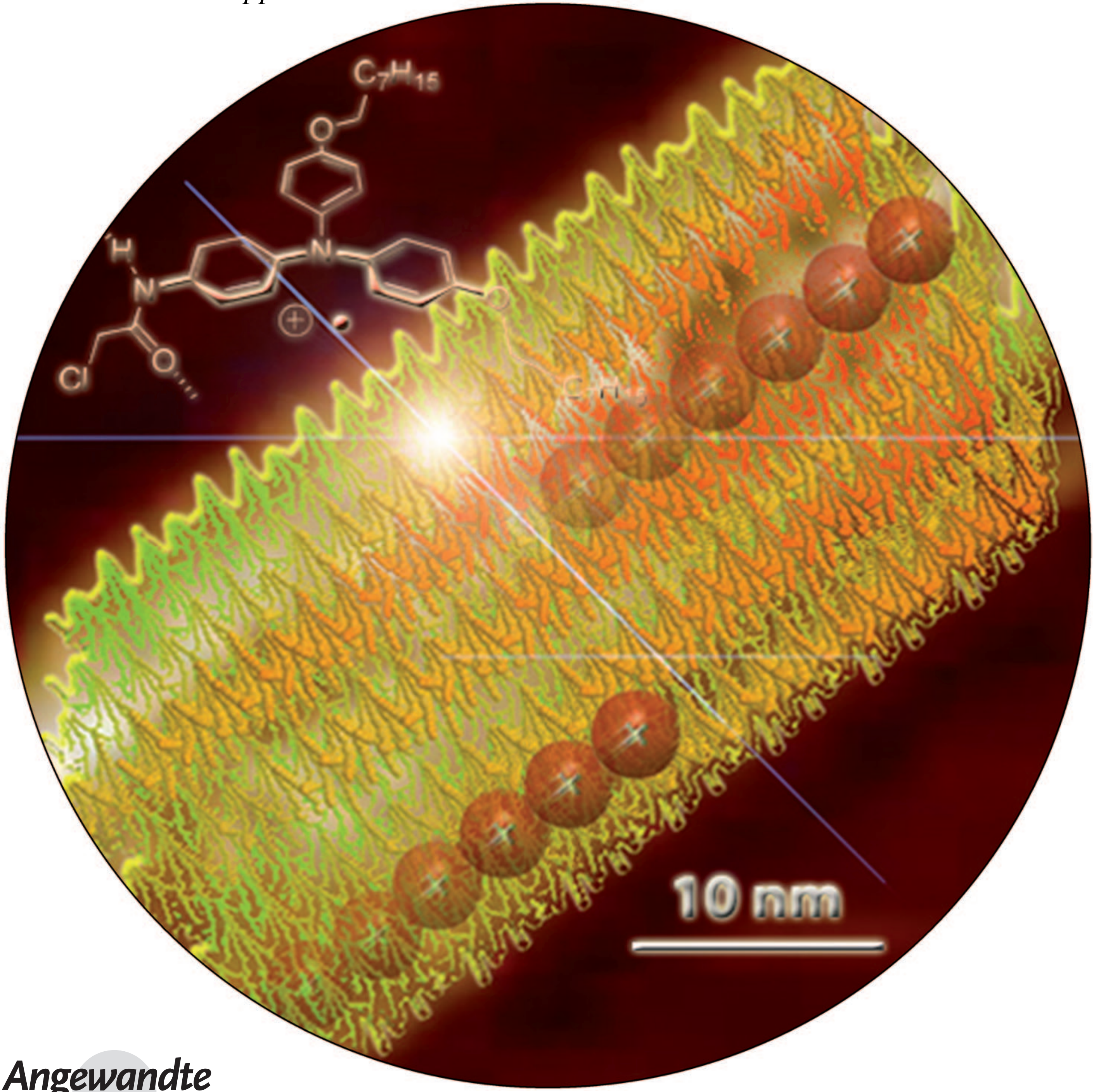
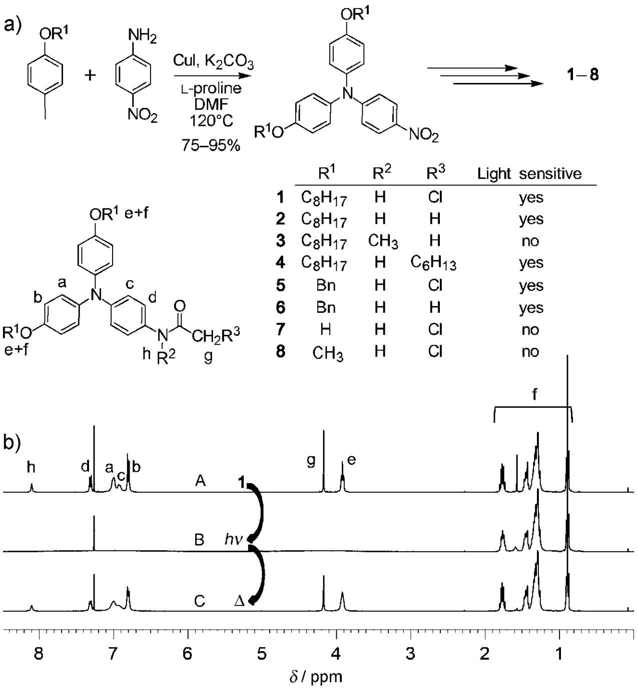


Angewandte Chemie

One of the most important goals for chemistry at the interface with materials and life science is to find new ways of building responsive functional systems at the mesoscale.[1–3] In this context, supramolecular chemistry has already proved to be a powerful approach to achieve precise control over self-assembled structures.[4–6] Indeed, the intrinsic reversibility of the interactions between the well-defined molecular units engaged in the formation of large supramolecular assemblies provides relatively defect-free and self-healing characteristics to these systems[7] and also makes them potentially responsive to a number of external stimuli.[8] For instance, organic photonic and optoelectronic materials have been shown to benefit from supramolecular self-assembly within highly organized aggregates such as vesicles,[9] nanotubes,[10] layers,[11] and other architectures, including the artificial photosynthetic systems developed by the research group of Wasielewski[12] and the supramolecular n/p-heterojunctions (SHJs) developed by Matile and co-workers.[13]

Triarylamine-type molecules are considered as very efficient functional units that are widely used as photoconductors and charge carriers.[14] In particular, these compounds display a high hole-transport mobility and are thus incorporated in optoelectronic devices[15] such as organic light-emitting diodes (OLEDs),[16] organic solar cells (OSCs),[17] organic field-effect transistors (OFETs),[18] and nonlinear materials,[19] and are even used as photoconductors for the Xerox process in laser printers and photocopiers.[20] However, despite the amount of studies performed on triarylamine derivatives, this molecular core has never been used as a structuring precursor that would be able to self-assemble into ordered supramolecular architectures, possibly with enhanced physical properties.

Recently, we observed the unique light-induced behavior of precursor **1** by ^{1}H NMR spectroscopy (Figure 1) in the course of investigations into the design of SHJs. Compound **1** was synthesized by using a modified Ullmann[21] one-pot coupling as a key process (see Figure 1a and the Supporting Information).



	R^1	R^2	R^3	Light sensitive
1	C_8H_{17}	H	Cl	yes
2	C_8H_{17}	H	H	yes
3	C_8H_{17}	CH_3	H	no
4	C_8H_{17}	H	C_6H_{13}	yes
5	Bn	H	Cl	yes
6	Bn	H	H	yes
7	H	H	Cl	no
8	CH_3	H	Cl	no

Figure 1. a) Structures and key synthetic step to access triarylamine derivatives **1**–**8**. b) Typical ^{1}H NMR spectra ($CDCl_3$) of **1** obtained immediately after purification (A); after 10 min exposure to visible light, (B); and after subsequent heating overnight at 60 °C (C); [**1**] = 10 mM.

Immediately after chromatographic purification, the NMR spectrum of **1** indicated the presence of the pure product (Figure 1b; spectrum A). Surprisingly, when the solution was exposed to natural light for a couple of minutes, a completely different spectrum was obtained (Figure 1b; spectrum B). In this spectrum, the complete disappearance of the aromatic protons (a–d), the aliphatic ether protons (e), and the acetamide protons (g,h), seemed to contradict the remaining resonance signals of the main aliphatic chains (f). Two observations were made at this stage: 1) the initial spectrum (A) was unchanged after one week in the dark, and 2) spectrum B, which was recorded after exposure of the sample to visible light, was also unchanged after one week in the dark. In addition, the color of the solution turned from light yellow immediately after purification into light green when exposed to light. The process was shown to be reversible by simply heating the solution of **1** in chloroform overnight at 60 °C. This observation was illustrated by the reappearance of protons a–e, g, and h (Figure 1b; spectrum C), and was accompanied by the loss of the solution's green color. No degradation of the product was observed by standard spectroscopic techniques after at least three light exposure/heating processes.

We subsequently studied the photophysical properties of a solution of **1** (1 mM) in chloroform by UV/Vis–NIR as a function of the irradiation time (the sample was irradiated with a 20 W white light between measurements). The spectra (Figure S1 in the Supporting Information) revealed the appearance of a new absorption band at 786 nm that was indicative of the production of a small quantity of the

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[**] We wish to thank the CNRS, the icFRC, and the University of Strasbourg for financial support. This work was supported by a doctoral fellowship of the French Ministry of Research (F.N.). We acknowledge the ESF-COST action on Systems Chemistry. We are also grateful to E. Aweke, S. Coulibaly, M. Bernard, and J. Raya for help at various stages.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201001833.

triarylammonium radical.[22] Similar results were obtained by irradiating solutions that were strictly deoxygenated by freeze–thaw cycles. To obtain quantitative data, EPR spectroscopy was performed on a nonirradiated solution, the ^{1}H NMR spectrum of which showed a full set of resonance signals (Figure 2a). As expected, no trace of radicals was detected in the dark ($t=0$; point A). However, after irradiating the sample with a white light (20 W) for one hour (A to B), the formation of a radical was clearly observed in a proportion of up to 11% compared to the total number of molecules (see the Supporting Information). The observed paramagnetic hyperfine pattern was consistent with that expected for a radical localized on the nitrogen atom of a triarylammonium derivative (see Figure S2 in the Supporting Information).[23] After one hour of irradiation, the amount of radicals was recorded as a function of time in the dark (Figure 2a; point B). A very smooth decay was observed over a period of 16 hours; the decay asymptotically reached a plateau at a concentration of 6 radicals per 1000 triarylamine molecules (points B to C). This concentration then remained constant for at least one week as verified by an EPR control experiment, thus reinforcing the idea of a radical-stabilization mechanism in the solution. Finally, the subsequent heating of the solution (point C) led to fast destruction of the remaining stabilized radicals over a period of 2 hours. This quantification of the radical confirmed its very low concentration at equilibrium and its unusual stability. As a consequence of the stability, the ^{1}H NMR spectra observed at equilibrium after light exposure (spectrum B in Figure 1b) might indicate that the total disappearance of the aromatic signals is not due to the presence of 6 paramagnetic species per 1000 molecules, but more likely caused by a self-association/delocalization process by charge transfer of these radicals when self-assembled with their neutral precursors. To test this assumption, we performed a high-resolution magic angle spinning (HRMAS) ^{1}H NMR experiment in solution; the possibly highly π-stacked aromatic parts of the molecules would behave as a very anisotropic domain in such an experiment and could be detected by averaging over the dipolar interactions. The observed reappearance of the resonance signals that disappeared after light exposure supports this claim, although an in-depth comparison between the two tensors of dipolar coupling and electronic paramagnetism did not allow for a definitive conclusion to assess the predominant phenomena (see Figure S3 in the Supporting Information). Importantly, chlorinated solvents appeared to be necessary to initiate the oxidation of the triarylamine. For instance, both the green color of the solutions and the disappearance of signals in the ^{1}H NMR spectrum also occurred when deuterated dichloromethane and 1,2-tetrachloroethane were used as solvents, but not when deuterated methanol, toluene, acetonitrile, or dimethylsulfoxide were used. These data are consistent with reported studies in which the excited state of the triarylamine can reversibly transfer one free electron to chloroform and liberate chloride counterions.[24–26]

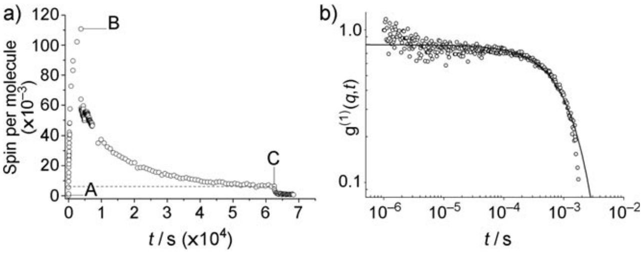

Figure 2. a) Quantitative EPR data, as a function of time, showing the evolution of the ratio of the triarylammonium radical $\mathbf{1}^{\cdot+}$ over neutral **1**: without visible light excitation at RT (point A); upon visible light excitation (A–B); in the absence of light at RT (B–C); and after subsequent heating (60°C) in the dark (from C; $[\mathbf{1}_{\text{init.}}]=10$ mM). Dotted line: y-axis value of 6×10^{-3}. b) Time autocorrelation function of the scattered electric field vector for an irradiated solution of **1** ($[\mathbf{1}_{\text{init.}}]=7.5$ mM in chloroform at $T=20$°C) and for a scattering angle $\theta=90°$. Solid line: exponential fit.

We then carried out a structure–property study by synthesizing derivatives **2–8** and investigating the sensitivity of their corresponding solutions in chloroform to light (see chart in Figure 1a). Here, the criterion of the response to light excitation was the disappearance (yes) or the persistance (no) of the NMR signals of the aromatic protons when the samples were submitted to irradiation for one hour. The results reveal that both the free N–H bond of the amide moiety (H-bonding interactions) and the long alkyl (or benzyl) R^1 chains must be present, thus indicating the requirement for additional van der Waals (or supplementary π-stacking) stabilizations of the hypothesized self-assembled structures.

We further investigated the solutions by dynamic light scattering (DLS) experiments (Figure 2b).[27,28] Prior to irradiation with visible light and consistent with previous observations, no evidence for the presence of assemblies or large objects could be deduced from DLS measurements on a solution of **1** in chloroform. However, after one hour of irradiation with visible light, the normalized time autocorrelation function of the concentration fluctuations, $g^{(1)}(q,t)$, could be characterized by a simple exponential relaxation (Figure 2b). The angular dependance revealed a diffusive relaxation with a characteristic time inversely proportional to q^2, where q is the scattered wave vector. In the case of a diffusive process, $g^{(1)}(q,t)$, is given by Equation (1):

$$g^{(1)}(q,t)=\frac{\langle\delta c(q,0)\delta c(q,t)\rangle}{\langle\delta c(q,0)^2\rangle}=\exp(-Dq^2t) \tag{1}$$

where $\delta c(q,t)$ and $\delta c(q,0)$ represent fluctuations of the concentration at time t and zero, respectively. The formation of self-assemblies in solution was thus demonstrated by the presence of this diffusive relaxation in the correlation function. In highly diluted solutions, the fit of $g^{(1)}(q,t)$ allows to determine the diffusive coefficient, $D=2\times10^{-12}\ \text{m}^2\text{s}^{-1}$, and, by using Equation (2), the average hydrodynamic radius can be determined, where η_w is the solvent viscosity.

$$R_H=\lim_{q\to0}\frac{k_BT}{6\pi\eta_wD} \tag{2}$$

In $CDCl_3$ ($\eta_w = 0.57$ cP at $T = 20$ °C), the apparent average hydrodynamic radius of the main species in dilute solution was found to be (180 ± 20) nm for $[\mathbf{1}] = 7.5$ mM. The DLS analysis and complementary neutron and X-ray scattering measurements showed that the assemblies are dense and polydisperse (see the Supporting Information).

We found AFM[29] (Figure 3) to be a key technique for the investigation of the self-assembled suprastructures. The irradiated green solution of **1** was quickly evaporated to dryness; the green residue obtained revealed the presence of highly organized structures.[30] Large fibrillar 3D aggregates (10–50 nm in width and 50–1000 nm in length) were observed in both height mode and phase mode (Figure 3a, and b, respectively). High-resolution scanning of these objects revealed their "corn-like" surface, which is composed of bundles of individual 1D fibers strongly packed in a concentric-layer organization (Figure 3c). For each individual 1D fiber, the separation between the bright dots was measured to be approximately (1.0 ± 0.3) nm in length. This distance is too large to represent the distance between individual stacked molecules; the dots might indicate a periodic pattern of triarylamines for which the lateral *p*-substituents would alternatively point into a particular direction (see Figure S6d,e in the Supporting Information for a suggested arrangement of the molecules). The lateral separation between two individual 1D fibers in the 3D aggregates was measured to be approximately (1.3 ± 0.4) nm, which is consistent with the dimensions of individual molecular wires made from the polymerization of a single row of triarylamine units. To correlate these structures with what was previously observed in solution, we then studied a liquid film deposited onto mica by spin coating of a 1 mM irradiated solution of **1** in chloroform (Figure 3d). While the resolution in the liquid state was lower than in the solid state, we observed the presence of a gel-like structure formed from dense entangled filaments, which can be precursors for larger and stiffer fibers at higher concentrations.

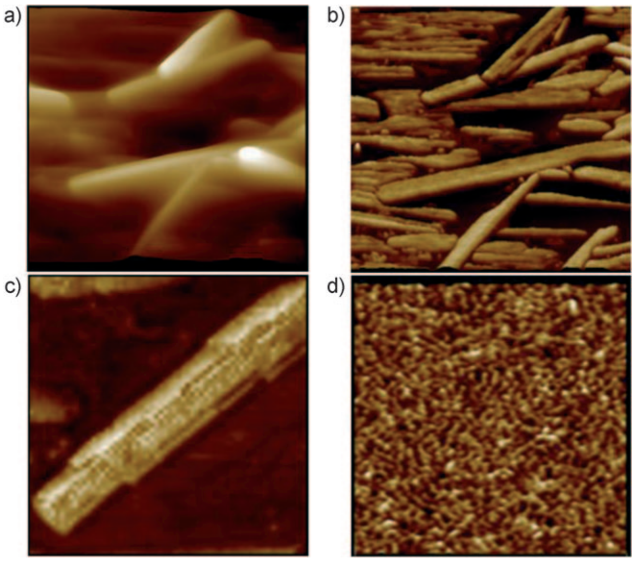

Figure 3. a) AFM height and b) phase images (surface scales 500×500 nm^2) of the self-assembled structures obtained by concentration to dryness of an irradiated solution of **1** in chloroform. c) AFM high-resolution image (surface scale 50×50 nm^2) of a single self-assembled structure obtained by concentration to dryness of an irradiated solution of **1** in chloroform. d) AFM image (surface scale 500×500 nm^2) of the self-assembled structures obtained by probing a liquid film made from an irradiated solution of **1** ($[\mathbf{1}_{\text{init.}}] = 1$ mM in chloroform).[30]

In conclusion, we have investigated responsive self-assembled suprastructures that are based on a triarylamine unit as a building block and react to light exposure. The self-assembly process occurs as a result of highly intriguing synergistic phenomena that start by the formation of triarylammonium cationic radicals upon stimulation with light (Figure 4). This radical can in turn be transferred to neutral triarylamines by charge hopping, thus allowing the supramolecular polymerization of units that contain a delocalized cationic radical. We also assume that, as indicated by EPR spectroscopy, one radical is sufficient to stabilize the stacking of about 160 triarylamine units along the long axis of the self-assembled wires. In addition to the charge-transfer phenomena and the π–π stacking interactions, the structure–property study revealed that at least one hydrogen bonding and van der Waals interaction of lateral chains should be combined to produce stable structures. Moreover, we have demonstrated that these molecular wires, which protect holes from quenching by the solvent, can combine into very strongly packed bundles of larger fibers.

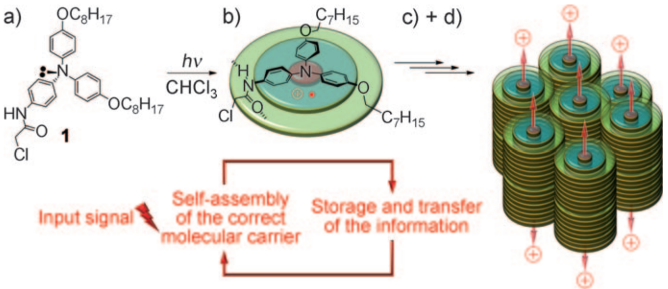

Figure 4. Hierarchical self-assembly processes that occur upon irradiation of the neutral triarylamine **1** (a). The electron transfer that occurs between light-excited triarylamines and the solvent produces a small amount of triarylammonium radical (b). In this electronic configuration, the charge transfer and various supramolecular interactions initiate the self-assembly of 1D supramolecular polymers (c) which combine to produce larger 3D fibers (d).

From a self-assembly point of view, this phenomenon represents a sort of "supramolecular living radical polymerization" process that can be triggered by charge transfer and be reversibly broken up by heating, because the radicals are spontaneously reduced by the solvent when they are not stabilized within the self-assembled structures. These results provide new insights into charge transfer self-assemblies and open a number of interesting possibilities by using these triarylamine synthons as new stimuli-responsive supramolecular scaffolds. From a functional point of view, such highly organized triarylamine-based architectures with enhanced physical properties (strong stabilization and hole conduction) might lead to both fundamental and applied investigations in the domain of organic materials for optoelectronics. Finally, from a conceptual point of view, such a system introduces a new approach for the circulation of information at the supramolecular level that would participate in the construction of "smart" materials. Indeed, the stimulation of this system with light (or an oxidant[26]) creates an electronic signal that induces the formation of the correct self-assembled carriers, that is, the supramolecular wires, which in turn are able to stabilize and transfer this first electronic signal over space and time. Thus, we have here a minimal example to understand and to design de novo stimuli-responsive chemical systems that display a fundamental synergistic and dynamic structure–function relationship, which consists of receiving, storing, conducting, and exchanging physical information by self-organization.

Received: March 28, 2010
Revised: June 9, 2010

Keywords: materials science · nanostructures · self-assembly · supramolecular chemistry · systems chemistry

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