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Light-Harvesting Hybrid Hydrogels: Energy-Transfer-Induced Amplified Fluorescence in Noncovalently Assembled Chromophore–Organoclay Composites**

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Light-harvesting and energy transfer between fluorescent donor and acceptor molecules have received increased attention in recent years because of their crucial role in photosynthesis and optoelectronic devices.[1] Since the supramolecular organization of donor and acceptor molecules is an important parameter in these photophysical processes, there has been an increasing interest in the design of various multichromophoric scaffolds.[2–8] The spatial organization of chromophores in an inorganic solid template appears to be advantageous, because such organic–inorganic hybrid materials would exhibit interesting optoelectronic properties coupled with enhanced mechanical properties.[9] In this context, silicate-based materials with their versatile structural chemistry and nanoscale periodicity could be a natural choice to host the chromophores for efficient light-harvesting. Recently, periodic mesoporous silica in which the walls were functionalized with fluorescent molecules[10] was shown to transfer energy to acceptor molecules organized in their mesochannels.[11] Clays are another class of layered silicate materials, whose interlayer galleries can be effectively utilized for hosting guest molecules for various applications.[12] However, the combination of chromophoric systems with inorganic clay layers is relatively unexplored and could be of great importance in hybrid optoelectronic devices.[13]

Of the various kinds of self-assembled structures, supramolecular gels[14] and the resultant nanostructures based on π-conjugated systems have been at the focus of much research effort over the last decade because of their potential applications in nanosized electronics.[15] Hydrogels[16] with fluorescent molecules have potential applications in biosensors and drug delivery as well, and only a very few rod–coil-shaped systems[17] have been used thus far as components of supramolecular hydrogels. However, designing highly fluorescent gels with optimal optical properties has been a challenge, often because of the fluorescence quenching associated with the aggregation of molecules.[18] Herein, we report the multicomponent self-assembly of novel clay–chromophore hybrids that form hydrogels, with aminoclay controlling the spatial distribution of the chromophores to result in fluorescence. While clay–polymer hydrogels are known in literature[19] this is the first report of the noncovalent interactions between clay layers[20] and fluorescent dye molecules being exploited for the design of hydrogels. We have also exploited organoclay as a template for the supramolecular organization of donor and acceptor molecules, which facilitates fluorescence resonant energy transfer. We further used the efficient light-harvesting between the chromophores anchored to the clay for the enhanced and controlled fluorescence of the resulting hybrids in solution, gel, and film states.

We have chosen amino group functionalized organoclay for the design of hybrid clay materials, since the functional amino groups can be exploited for the noncovalent attachment of the chromophore molecules. The aminoclay (**AC**) used herein is a layered magnesium organosilicate having a structure analogous to 2:1 trioctahedral smectites with an approximate composition of $R_8Si_8Mg_6O_{16}(OH)_4$, where R represents covalently linked aminopropyl substituents (Figure 1).[21] The repulsion between the layers due to the

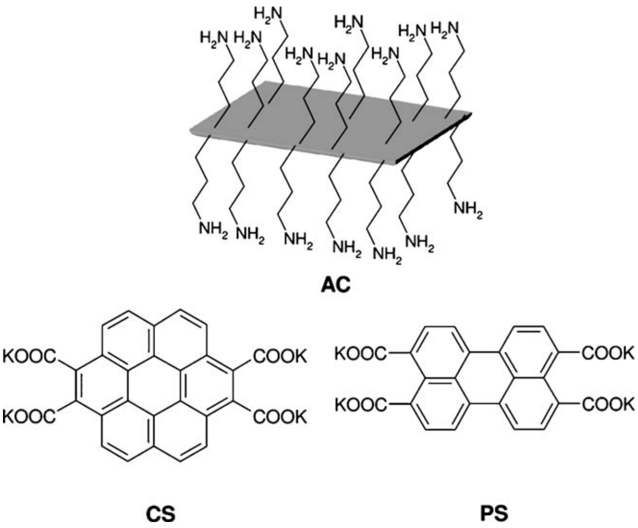

Figure 1. Chemical structures of a single layer of aminoclay (**AC**) and anionic dyes (**CS** and **PS**).

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protonation of amino groups in water makes this clay easily exfoliable even at higher concentration, leading to a clear solution. The chromophores we have used here for the noncovalent functionalization of aminoclay are potassium tetracarboxylates of coronene and perylene (Figure 1), referred to as coronene salt (**CS**) and perylene salt (**PS**), as they have high fluorescence quantum yields and high solubility in water.[22] The negatively charged carboxylate groups of these dyes are expected to interact electrostatically with the positively charged aminoclay in water, thus resulting in noncovalent hybrid materials. **CS** and **PS** show absorption maxima at 314 and 469 nm, whereas they emit in the blue ($\lambda_{max} = 435$ nm) and green ($\lambda_{max} = 481$ nm) regions in water, respectively.[23]

First we investigated the individual interaction of the **PS** and **CS** with clay in water. Spectroscopic titration experiments of the **PS** ($c = 10^{-4}$ M, 1 mL) with a stock solution of **AC** in water (1.0 wt %) initially showed a decrease in the absorbance accompanied by concomitant scattering, broadening, and a red-shift in the absorption maxima (469 nm to 474 nm, up to 0.03 wt % of **AC** in the final solution) owing to the interaction between the clay and dye molecules (Figure 2a). Further addition of **AC** (≥ 0.05 wt %), however, reversed this trend without any further changes in the red-shifted absorption maxima at 474 nm. A complete recovery of the absorption intensity equivalent to the pure **PS** was observed when the **AC** content in the final solution reached 0.3 wt %. A similar trend was observed in the fluorescence behavior of **PS**, although to a different extent upon addition of **AC**. For example, **PS** solutions containing 0.03–0.1 wt % of the clay were almost nonfluorescent and only 25 % of the original emission intensity was regained even at the higher concentration of clay (> 0.3 wt %, corrected emission spectra for optical density, Figure 2b). Furthermore, the recovered dye emission maxima at higher clay concentrations (> 0.3 wt %) are red-shifted by an additional 3 nm (481 nm to 484 nm) relative to the emission maxima of pure dye molecules or dye with lesser amount of clay. These optical changes suggest the presence of two different states for clay–dye hybrids in which the molecular organization of the individual components could be different. At the initial stages, when the amount of **AC** is less, the aggregation and cross-linking of large number of **PS** molecules interacting with each layer of clay would lead to the clustering of clay hybrids (we designate it as State-A, Figure 2c) and hence results in the decrease of absorption and emission intensity. The clustering of the clay hybrids in State-A is further supported by the observation of the visible settling of clay–dye hybrid flakes with time as well as by the scattering observed in the UV/Vis spectra. However, when the amount of clay is increased for the same concentration of **PS** (1×10^{-4} M), the density of dye molecules sticking to each layer of clay would be reduced (designated as State-B, Figure 2c) mimicking more or less the condition of exfoliated clay layers with dangling dye molecules, and hence the absorption and fluorescence are increased in intensity. The titration of **CS** with **AC** showed a similar trend in optical properties.[23] The particle size measurements carried out using DLS over these two sets of clay–**PS** hybrid solutions further proved the difference in their molecular organization.[23] The very broad and larger size distribution obtained for the solution with the low clay amount is consistent with the presence of large aggregated structures. On the other hand, the solution with higher clay amount showed a narrow distribution and smaller size, which closely matches with the size distribution observed for the exfoliated clay sheets. The molecular organization of the **AC**–**PS** hybrids in solution were also retained in the solid-state as evident from the optical, powder X-ray diffraction (PXRD), and transmission electron microscopy (TEM) studies of the precipitates obtained from different states by the addition of ethanol.[23]

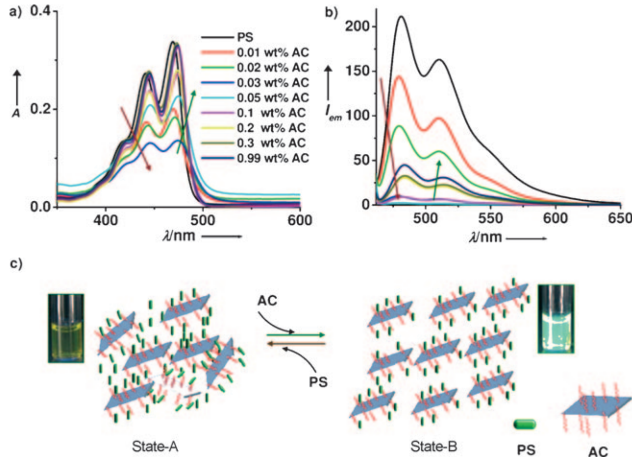

Figure 2. Changes in a) absorption and b) emission spectra of **PS** on spectroscopic titration with **AC** ([**PS**] = 1×10^{-4} M, $l = 1$ mm, $\lambda_{exc} = 450$ nm). The red and green arrows show the gradual formation of State-A and State-B, respectively. c) Schematic representation of different states of **AC**–**PS** hybrids in solution and the photographs of corresponding solutions of hybrids under UV light.

Interestingly, when the concentration of dyes (**CS** or **PS**) and **AC** is increased (ca. 100 times) by keeping the ratio between them similar to State-A (10^{-4} M dye: 0.1 wt % **AC**) in water, highly stable transparent hydrogels were formed, which is confirmed by an inverted vial method.[23] In a typical experimental procedure, the precipitate formed by mixing the aqueous solutions of dye (**CS**/**PS**) and the clay was sonicated until the solution became clear and then left at room temperature. Stable, self-standing hydrogels were formed within 20 min, which further confirmed the cross-linking nature of the dyes in State-A. The critical gelator concentrations were found to be 7.5×10^{-3} M (**AC** 7.5 wt %) for **CS** and 5.0×10^{-3} M (**AC** 5.0 wt %) for **PS**, which suggested a stronger cross-linking interaction of **PS** with **AC**. The total wt % of the hybrid components in case of **CS**–**AC** and **PS**–**AC** gel is nearly 12.0 and 8.0, respectively, suggesting the high water content in the hydrogels. Although hydrogels were formed with high efficiency, they are weakly fluorescent due to the intermolecular interactions between the chromophores in State-A.[23] **CS**–**AC** and **PS**–**AC** hybrid hydrogels show weak blue ($\lambda_{max} = 440$ nm, $\lambda_{exc} = 350$ nm) and greenish-yellow ($\lambda_{max} = 516$ nm, $\lambda_{exc} = 450$ nm) fluorescence, respectively. The decrease in fluorescence intensity along with the red-shift in the emission maxima (2–3 nm) of the dyes in the hybrid gels compared to that of State-A solution suggests strong intermolecular interaction between the dyes. Moreover, in the **PS–AC** hybrid gel, the higher intensity of the emission band at 516 nm compared to the high-energy band at 487 nm along with the appearance of the new broad band around 600 nm is characteristic of the J-aggregation of perylene chromophores.[15c] The clay to dye ratio in State-A is also found to be very crucial for the formation of the gels, as higher clay to dye ratio failed to produce gels at any concentration.

We extended the exploration of the efficiency of aminoclay as a novel class of supramolecular templates to include photo-induced Förster resonant energy transfer (FRET) between donor and acceptor chromophores that are non-covalently anchored onto the clay surface. Since the FRET process involves a through-space dipole–dipole interaction, the ordered aminopropyl groups on the clay nanosheets are expected to provide an efficient scaffold to orient the donor and acceptor molecules in the mixed chromophore clay hybrids and to facilitate energy transfer. Furthermore, efficient energy transfer to fluorescent acceptor molecules in mixed chromophoric clay hybrids would also help the design of luminescent hybrids even in the gel/solid phases, compared to the quenched fluorescence of individual dye–clay gels.[5e] The emission spectrum of **CS** (donor, 425–500 nm) has a very good spectral overlap with the absorption bands of the **PS** (acceptor, 380–500 nm), and hence an efficient Förster-type energy transfer between **CS** and **PS** can be envisaged, if there is a proper spatial orientation between the chromophores.[23] Furthermore, the well-separated absorption bands of the donor and acceptor molecules ensure that both the **CS** and **PS** molecules can be selectively excited at 350 and 450 nm, respectively, in mixed chromophore hybrids which would help to analyze the energy transfer efficiencies.[23] A comparison of the absorption spectra of the mixture of dyes with **AC** or in the absence of **AC** showed characteristic bands of the individual chromophores and hence ground-state interaction between the dyes is ruled out.[23]

Despite the good overlap of the emission of **CS** with the absorption of **PS**, no energy transfer was observed from **CS** (1×10^{-4} M) to **PS** (1×10^{-5} M, 10 mol% relative to **CS**) in the absence of clay sheets, suggesting the lack of spatial ordering due to the molecularly dissolved nature of the dye molecules in water.[23] We first investigated the feasibility of energy transfer in mixed **CS–PS**–clay hybrids in aqueous solution. Hence, mixed chromophore–clay hybrids were prepared with various donor–acceptor compositions, by keeping the clay to **CS** (donor) dye ratio similar to that in State-B (10^{-4} M dye: 0.8 wt% **AC**) where the clay sheets are completely exfoliated and are highly fluorescent. When the mixed chromophore–clay hybrid sheets are excited at 350 nm (the donor, **CS** absorption), quenching of the donor emission between 450–500 nm could be seen, with the concomitant increase in the **PS** emission at 500–600 nm, indicating the excitation energy transfer from the coronene to perylene chromophores (Figure 3a). Energy transfer from the coronene to perylene chromophore when anchored to the clay sheets was further confirmed by the direct excitation of the **PS** at 350 nm in the absence of **CS** which showed negligible emission. Furthermore, the excitation spectra collected at the **PS** emission ($\lambda_{em} = 515$ nm) in the mixed chromophore–clay hybrids match the absorption spectra of **CS**, which provides an unambiguous proof of the energy-transfer process.[23] However, a significant amount of **CS** emission remains even up to 10 mol% loading of the acceptor **PS** dyes indicating a less efficient energy transfer. For further understanding of the mechanism of energy transfer we have carried out a titration experiment with increasing amounts of **AC** keeping the concentration and composition of the donor and acceptor chromophores constant (**CS** containing 10 mol% of **PS** at 1×10^{-4} M, Figure 3b). Energy transfer was monitored by normalizing the emission spectra at the donor emission, and then plotting the increase in acceptor emission between 475–600 nm as a function of clay concentration. More efficient energy transfer was observed when the dyes are anchored to 0.1 wt% of **AC** which corresponds to State-A. Further increase in clay concentration above 0.1 wt% led to a gradual decrease in the energy transfer and became less efficient in State-B (0.8 wt% **AC**). Hence it is evident that the low energy-transfer efficiency in State-B could be either due to the absence of any interclay excitation energy transfer as the clay sheets are fully exfoliated or the donor chromophores in the clay sheets are too sparsely dispersed to provide efficient light-harvesting. Energy-transfer efficiencies at different states were calculated by comparing the excitation spectra ($\lambda_{em} = 515$ nm) with corresponding absorption spectra normalized at the λ_{max} of the acceptor perylene dye, and the

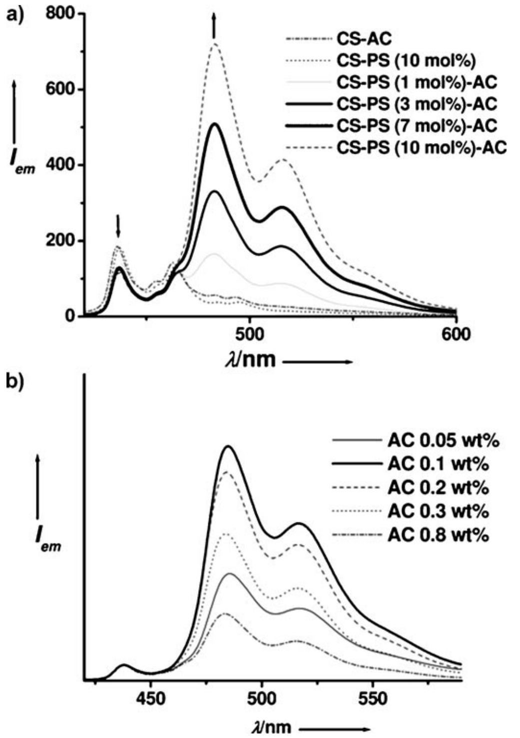

Figure 3. a) Fluorescence titration spectra of **CS–AC** hybrids in State-B (**CS** = 1×10^{-4} M, **AC** = 0.8 wt%, $\lambda_{exc} = 350$ nm) with different amounts of **PS** and b) normalized emission spectra at donor emission for different amounts of **AC** (**CS** = 1×10^{-4} M, **PS** = 10 mol%, $\lambda_{exc} = 350$ nm) in water.

efficiencies in State-A and State-B are found to be 50 and 10%, respectively.[23] Remarkably, in State-A of the mixed hybrids (10 mol% of **PS**), excitation of the donor, **CS**, at 350 nm gives 11 times higher **PS** emission due to energy transfer compared to the direct excitation of the acceptor **PS** at 450 nm.[23] This amplified emission is a definitive proof of a Förster-type energy-transfer mechanism and an antenna effect in light-harvesting. We further thought of using the FRET as a probe to investigate the dynamics of the molecules in the hybrid dye–clay systems. With this purpose we introduced the acceptor **PS** molecules to **CS–AC** hybrid aqueous systems and the kinetics of the evolution of **PS** emission by energy transfer was monitored. Interestingly, the **PS** emission due to energy transfer was completely attained within the measurement time (< 1 min) in both State-A and State-B, suggesting a very fast dynamics of the molecules in the clay hybrids.

To further investigate the scope of energy transfer between the dyes organized in the clay matrix for the design of fluorescent hybrid gels we performed studies with mixed chromophore–clay gels. Mixed chromophore–clay gels were prepared with various donor–acceptor compositions (0–50 mol% of **PS** relative to **CS**) by the incorporation of required amounts of **PS** into the aqueous solution of **AC** containing **CS** at its critical gelator concentration. The mixture was further sonicated and kept at room temperature to form corresponding hybrid gels. Upon excitation of the hybrid gels at 350 nm, the emission intensity at 440 nm showed a gradual decrease, with the concomitant generation of a green emission at 485 nm, as the **PS** loading increases, suggesting energy transfer (Figure 4a). This green emission through energy transfer is remarkable, as the corresponding pure **PS–AC** gels are virtually nonfluorescent (Figure 4a).[23] However, at lower percentages of acceptor, **PS** (1–5 mol%), the acceptor emission at 475–600 nm was greater when **PS**

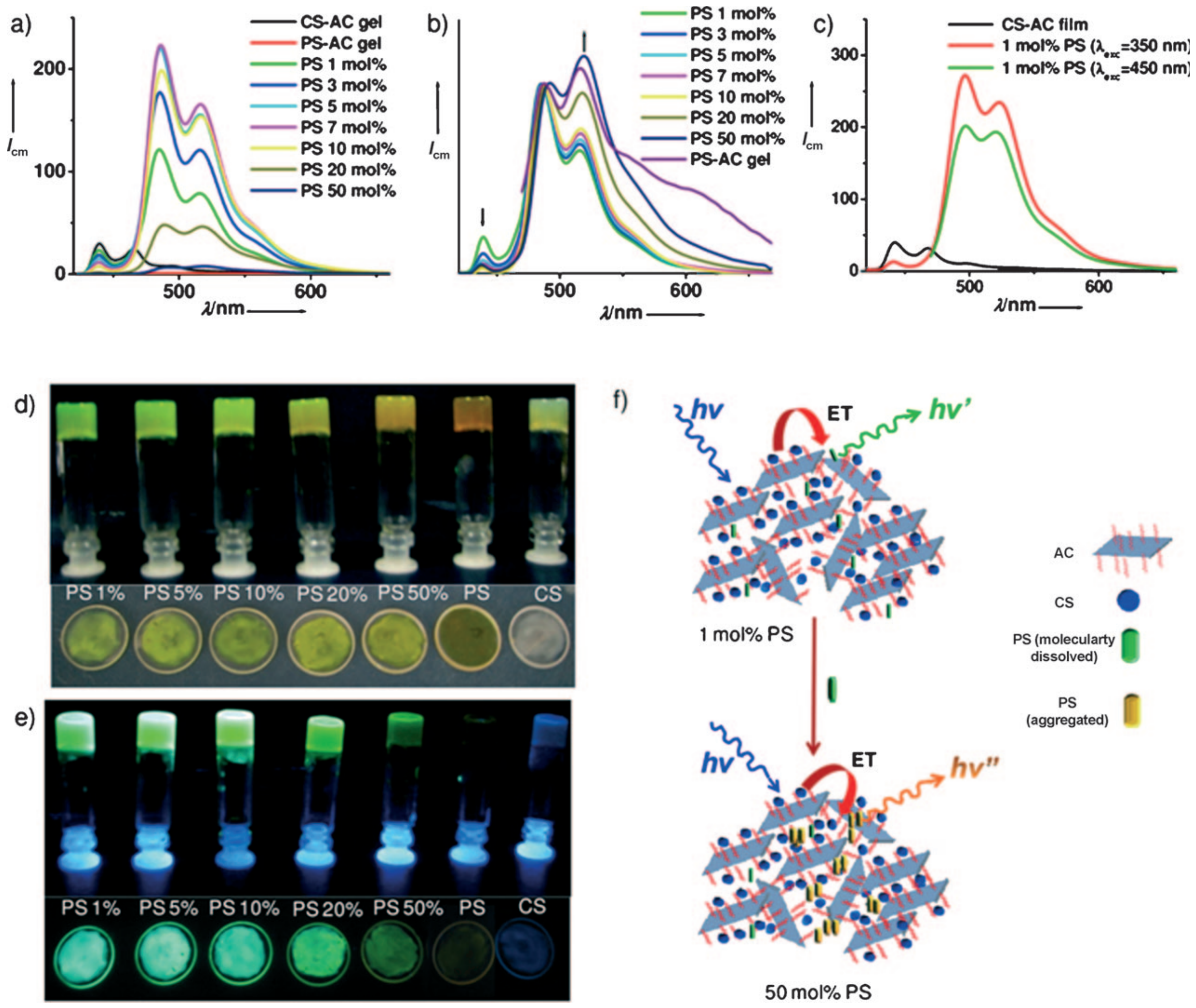

Figure 4. a) Emission spectra due to energy transfer in hybrid gels ($\lambda_{exc} = 350$ nm, $l = 1$ mm). b) Normalized emission spectra of hybrid **CS–PS** gels with different amounts of **PS**, showing the interaction between the **PS** chromophores ($\lambda_{exc} = 350$ nm, $l = 1$ mm, $\lambda_{norm} = 487$ nm). c) Emission spectra of hybrids **CS** and **CS–PS** xerogels dried on quartz plates. d,e) Photographs of hydrogels and corresponding films on quartz plates, made from both individual and mixed dyes with **AC** under d) visible and e) UV light. The mol% of **PS** is relative to **CS**. f) Schematic representation of the self-assembly and energy transfer in clay–dye hybrid gels.

was directly excited at 450 nm, indicating the absence of antenna effect.[23] Further loading of the **PS** (> 7 %) results in amplified green emission from the gels due to energy transfer and the fluorescence reaching a maximum. However, increase of **PS** concentration above 10 % results in decrease of fluorescence at 485 and 515 nm with a simultaneous bathochromic shift indicating the interaction between the perylene chromophores. Interaction between the chromophores in hybrid hydrogels at higher percentages of **PS** is further evident from the normalized emission spectra at 485 nm, which showed a gradual increase in the intensity and red-shift of the emission band at 515 nm and the appearance of a broad emission around 600 nm, characteristic of the perylene chromophore stacking (Figure 4 b). This indicates that at low **PS** loadings, the acceptor molecules exist as isolated energy traps resulting in highly intense green emission from individual perylene chromophores. On the other hand, at higher **PS** loadings the acceptor molecules are able to interact with each other resulting in aggregate energy traps with lower energy to give red-shifted emission with low quantum yield (Figure 4 d–f).[5e] Since efficient energy transfer in the solid films is a prerequisite for the device applications, we have extended the studies to the films made from the gels (xerogels) which showed the same fluorescence trend as the gels.[23] Remarkably, the films with even 1 % of **PS** showed a significant quenching of the donor emission and an enhanced fluorescence intensity due to energy transfer compared to the direct excitation of the acceptor (Figure 4 c), suggesting very efficient light-harvesting. This significant amplified emission through energy transfer in the film state is unprecedented and shows the remarkable efficiency of clay–dye hybrids as novel supramolecular scaffolds for energy transfer.[23]

In conclusion we have demonstrated the design of a novel class of aminoclay–dye fluorescent hybrids and hydrogels by a simple noncovalent self-assembly approach. We have described that control of nanoscale organization through an organic–inorganic hybrid approach provides an efficient strategy for tailoring the macroscopic and optoelectronic properties of organic chromophores. Furthermore, the combination of the dynamic nature of the noncovalent hybrid networks with the possibility to incorporate a variety of molecules that can trigger the fluorescence changes in the hydrogels holds great promise for applications as stimuli-responsive supramolecular systems and sensors.

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