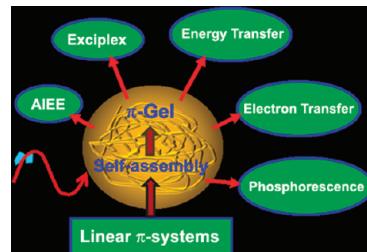


Excited State Processes in Linear π -System-Based Organogels

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ABSTRACT This article describes the recent progress made to the understanding of the excited state interactions in organogels derived from linear π -conjugated molecules. The soft organogel scaffolds of such systems create an excellent ambience for the self-organization of the molecules allowing the modulation of their excited state properties and thereby opening a new world of fascinating materials with interesting physical properties at nano- and macroscopic levels. Noncovalent interactions provide opportunity for the molecules to interact electronically within a space of defined size and shape. As a result, the photophysical properties of the molecules in solution and gel states are different from each other. In this perspective article we analyze the role of the self-assembled organogel scaffolds of π -gels derived from linear π -systems in modulating the excited state properties such as excited state energy transfer, exciplex emission, phosphorescence, and aggregation-induced enhanced emission (AIEE), when compared to the corresponding individual molecules.



In recent years there has been significant interest in chromophore based self-assemblies due to their potential application in organic electronics.^{1–4} It is of particular interest to organize the chromophores in a regular array to improve the optical and electronic properties.^{5,6} In this context, organogelation is recognized as a powerful tool to develop new functional materials.^{7,8} The design strategy with a priori knowledge of the possible modes of aggregation offers a working model with which one can explain the successes and failures of gelation processes.^{9,10} In such a design, the geometry of the building blocks, the spatial arrangement, and the nature of the intermolecular interactions will determine the structure and properties of the supramolecular aggregate of different chromophoric systems.^{5,11,12}

In most of the supramolecular gels, entangled networks of fibers are formed by the self-assembly of molecules using different noncovalent interactions such as hydrogen bonding, π -stacking, van der Waals interactions, and so forth in a quasi one-dimensional (1D) manner.^{13,14} Organogelation brings significant changes in the photoluminescence properties, which could not be observed in the respective monomers and, hence, accomplish several fundamentally important processes such as energy or electron transfer in a more viable way.^{11,12,15} The luminescence property eventually depends on how the molecules are packed in the aggregates, rather than being an intrinsic property of the material. In this context, it should be noted that the nature of solvents in which the organogels have been formed is crucial to the self-assembly of the molecules, which in turn will control the intermolecular interactions, and thereby tune the optical properties. In a precise and controlled growth process, the spectral features of photoluminescence can be correlated to

structural topologies of the system. As a consequence, photophysical phenomena such as energy and electron transfer, excimer and exciplex formation, aggregation-induced enhanced emission (AIEE), and related processes can be remarkably controlled, which significantly modulates the emission properties in the organogel state. In the following, we will analyze some of the recent progress associated with these phenomena.

The luminescence property of the self-assembly depends on how the molecules are packed in the aggregates, rather than being an intrinsic property of the individual molecules.

Excited State Energy and Electron Transfer Processes. Spatial arrangement of donor and acceptor molecules is important to achieve efficient energy and electron transfer between molecules.^{16,17} Organogels derived from donor–acceptor molecules have been proven as efficient media to promote energy-transfer

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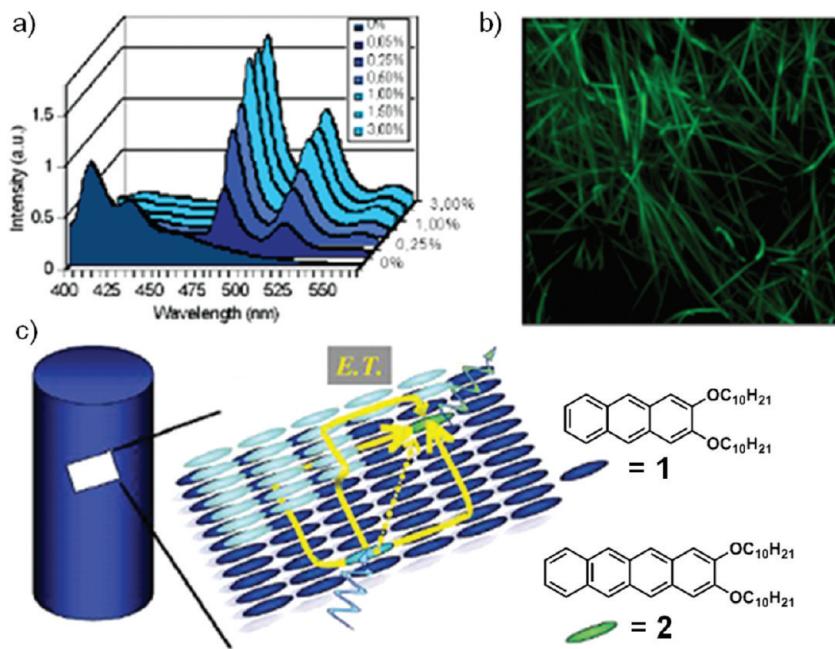


Figure 1. (a) Emission spectra of the DMSO gel of **1** ($\lambda_{\text{exc}} = 384 \text{ nm}$) doped with increasing proportions of **2**, (b) fluorescence confocal microscopy image ($50 \times 50 \mu\text{m}$) of the DMSO gel of **1** at 298 K with $2 \text{ mol } \%$ of **2** ($\lambda_{\text{ex}} = 405 \text{ nm}$) and (c) schematic representation of a doped gel fiber of **1** as well as energy transfer pathways. Reprinted with permission from ref 20. Copyright 2005 American Chemical Society.

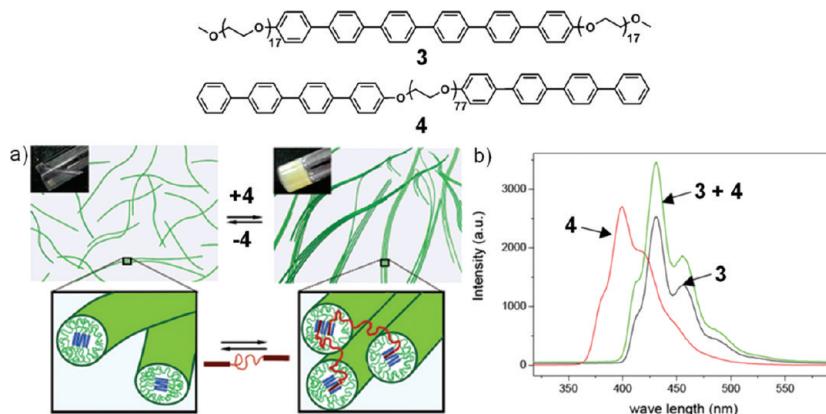


Figure 2. (a) A cartoon representation of the reversible bridging between the isotropic fluid and the nematic gel of the supramolecular nanocylinders. (b) Fluorescence spectra of the aqueous solution of **3**, **4**, and coassembly of **3** (0.1 wt %) and **4** ($\lambda_{\text{ex}} = 290 \text{ nm}$). Reprinted with permission from ref 21. Copyright 2005 American Chemical Society.

processes.^{11,12} The choice of a donor and an acceptor with suitable optical and self-assembly properties is therefore extremely important in the design of organogels that allow facile excitation energy transfer.^{11,18,19} However, it is important to identify molecular donor–acceptor systems that self-assemble to form gels, in which the excited state properties of the donor and the acceptor could be exploited to control the photophysical properties of the gel matrix. With this objective, a variety of chromophores, both functional organic dyes as well as π -conjugated fluorophores, modified with functional groups that interact through noncovalent forces have been reported.^{8,9,11,12}

One of the efficient energy transfer systems based on organogels is reported with 2,3-*n*-didecyloxyanthracene **1** as

the excitation energy donor and 2,3-*n*-didecyloxytetracene derivative **2** as the acceptor.²⁰ A dimethyl sulfoxide (DMSO) gel of **1** containing 1 mol % of **2** exhibits almost total quenching of the emission of **1** with a concomitant increase in the emission of **2** with a 100 nm Stokes shift (Figure 1a). The incorporation and uniform dispersion of the acceptor in the donor fiber was confirmed by the fluorescence confocal microscopy image of the mixed gel (Figure 1b). Detailed energy transfer studies revealed that the efficiency of the process is highly influenced by the structural and chemical similarity between donor and acceptor, which leads to parallel orientation of the dipoles of the chromophores as well as the involvement of exciton migration in the donor gel scaffold (Figure 1c). Efficient energy transfer with less than 1 mol % of

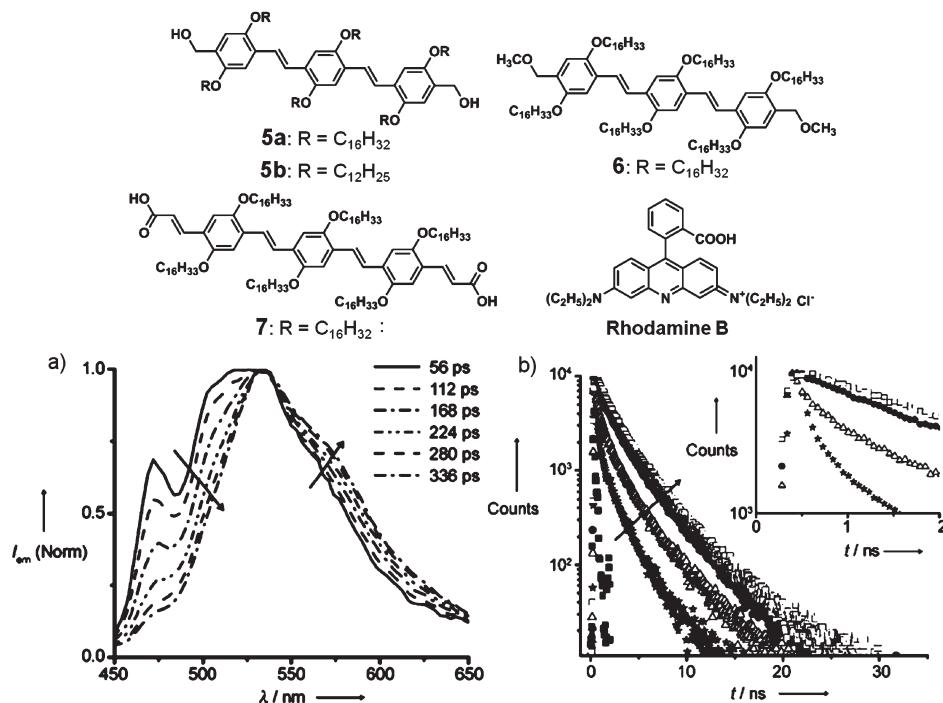


Figure 3. (a) TRES of **5a** gel in cyclohexane. (b) Wavelength-dependent emission decay curves of the **5a** gel; inset shows the initial growth in the emission decay of the **5a** gel after short time periods: instrument response function (IRF) ■; 478 nm, ●; 504 nm, Δ; 536 nm, ◆; 574 nm, □ ($c = 4 \times 10^{-4} \text{ M}$, $l = 1 \text{ mm}$, $\lambda_{\text{ex}} = 375 \text{ nm}$). Reprinted with permission from ref 28. Copyright 2007 Wiley-VCH.

the acceptor strongly supports the role of the gel phase in facilitating fast exciton migration within the gel fibers and is an example of a supramolecular light harvesting system.

The self-assembly of amphiphilic triblock coil–rod–coil molecule **3** in the presence of a small amount of the rod–coil–rod molecule **4** leads to the formation of anisotropic gel (Figure 2a).²¹ The anisotropic gelation was observed as a result of the formation of bundles of the cylindrical micelles aligned in a parallel fashion as observed in the transmission electron microscopy (TEM) images. The excitation of the coassembly at 290 nm resulted in strong emission from **3** at 431 nm (Figure 2b). In this case, most of the radiation is absorbed by **4**, and an emission corresponding to **3** with a concomitant quenching of the emission of the former is observed. These results indicate that energy transfer takes place from **4** to **3**, which is additional evidence for the formation of the coassembly between these two molecules.

A class of organogelators that exhibit efficient energy transfer in the gel phase is oligo(*p*-phenylenevinylene)s (OPVs). A number of OPVs with different end functional groups and lateral side chains were synthesized and shown to form organogels with tunable emission colors.^{22–32} An interesting feature of OPV gels is the large red-shift in the emission at the gel phase when compared to that in the solution phase. Time-resolved emission studies (TRES) have shown that this shift in the emission maximum is due to the efficient exciton migration within the aggregates of different highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO–LUMO) levels (Figure 3a).²⁸ The wavelength-dependent emission decay of **5a** in the gel state indicated that emission at the shorter wavelength (478 nm) decays faster than that at the higher wavelength (Figure 3b) and exhibited a delayed growth

(Figure 3b; inset) within the initial short time periods. Therefore, the migration of excitons from higher to lower energy aggregates results in a red-shift in the wavelength.

Energy transfer between OPV (**5–7**) gels and the encapsulated rhodamine B was one of the early reported cases in the gel state.^{23,25} However, due to the noncompatibility of the acceptor with the donor gel, the energy transfer efficiency was found to be low in this case. Subsequently, better energy transfer systems were designed using a series of OPVs (**8–11**) (Figure 4) with suitably different HOMO–LUMO energy levels of the donor and the acceptor.²⁹ The tuning of emission at the molecular level and the modulation of the gelation behavior at the supramolecular level were obtained by the rational choice of dipolar end functional groups in OPVs. The emission of **8** and the absorption of **11** showed a good overlap (spectral overlap integral, $J(\lambda) = 1.90 \times 10^{15} \text{ nm}^4 \text{ M}^{-1} \text{ cm}^{-1}$). Energy transfer studies have revealed that, in the presence of 2.62 mol % of the acceptor **11**, a gel of **8** in *n*-decane showed 90% quenching in the fluorescence intensity with a concomitant increase in the emission of the acceptor ($\lambda_{\text{ex}} = 380 \text{ nm}$) (Figure 4a). A 3-fold increase is observed in the luminescence of **11** after energy transfer when compared to that of direct excitation ($\lambda_{\text{ex}} = 495 \text{ nm}$), which indicates efficient energy transfer in this system (Figure 4a; inset). The fluorescence decay profiles of **8** in the presence of different mole percent of added **11** exhibited an acceleration of the decay process (Figure 4b).

A supramolecular light harvesting system with control over supramolecular assemblies of donor and acceptor systems resulting in tunable emission was demonstrated using OPV **10** (Figure 4) as the acceptor and gelator **12** (Figure 5) as the

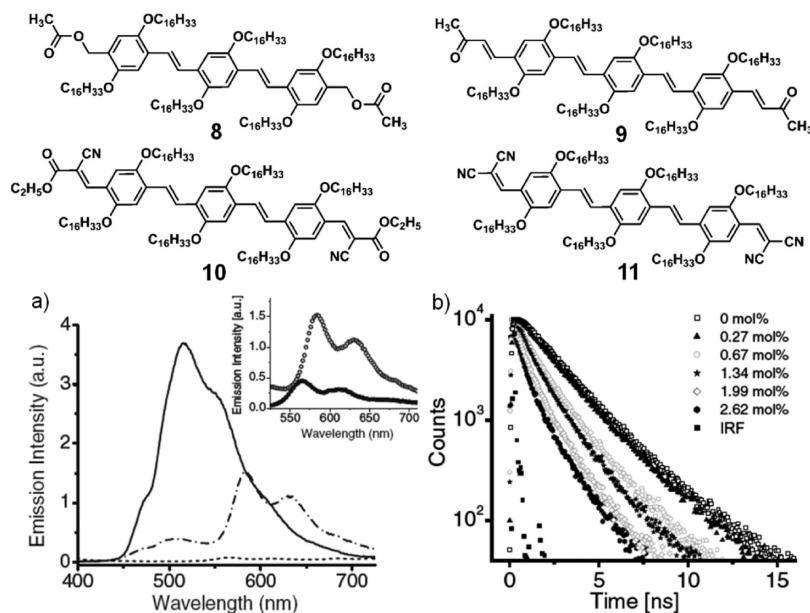


Figure 4. (a) Emission spectra of **8** in the absence (—) and in the presence (−·−) of **11** (2.62 mol %) in *n*-decane; emission of acceptor in the absence of donor (---). Inset shows the emission of the acceptor upon indirect excitation at 380 nm (○) and direct excitation at 495 nm (●). (b) Lifetime decay profiles of **8** on addition of different amounts of **11**, $\lambda_{\text{ex}} = 375$ nm in *n*-decane gel (4×10^{-4} M); emission monitored at 516 nm. Reprinted with permission from ref 29. Copyright 2007 Wiley-VCH.

donor.³⁰ Coassembly of **10** and **12** facilitates the controlled self-location of **10** within the coassembly. Hence, excitation of donor gel in *n*-decane at 380 nm in the presence of 0–2 mol % acceptor **10** resulted in the quenching of the donor emission at 509 nm with a concomitant formation of the monomer emission of the acceptor at 555 nm. In contrast, upon increasing the amount of **10** from 2 to 20 mol %, formation of statistically distributed aggregates with different HOMO–LUMO gaps provide an energy gradient resulting in the funneling of the excitation energy to higher order aggregates of **12** leading to a red-shifted emission at 610 nm with 98% quenching of the donor emission at 509. Fluorescence lifetime decay profiles ($\lambda_{\text{ex}} = 375$ nm) showed an accelerated decay of the donor fluorescence in the presence of the acceptor due to the population of the acceptor excited states before it decays by radiative mechanism. This study demonstrates an efficient trapping of excitons by “isolated” or “aggregated” acceptors leading to a gradually tunable emission color between green and red (λ_{max} , 509–610 nm).

An organic supramolecular light-harvesting system comprising an OPV gel as the donor and a π -conjugated molecular wire as the acceptor exhibits efficient energy transfer in the organogel scaffold.²⁸ The broad absorption band observed for the cyclohexane solution of the acceptor **13** (6.12×10^{-6} M) (Figure 5) overlaps well with the emission of the self-assembled donor **5a**, with a spectral overlap integral of $J(\lambda) = 5.83 \times 10^{15} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$. The feasibility of energy transfer has been studied in the gel state by encapsulation of small quantities of **13** (0–1.53 mol %) within the self-assembled structure of the donor **5a** in cyclohexane (1.12 mM). Efficient energy transfer at low mole percent of the acceptor (< 1.6 mol %) due to the fast exciton migration ($k_{\text{EM}} = 1.28 \times 10^{10} \text{ s}^{-1}$) of the singlet exciton within the gel medium was observed

(Figure 5a). The rapid decay of the higher energy shoulder bands and the dynamic red-shift of the emission within short time periods indicates the importance of fast exciton migration from low-order aggregates (higher energy sites) to higher order aggregates (lower energy sites) of the **5a** gel. The biexponential fluorescence decay profile of **5a** gel in cyclohexane ($\tau_1 = 1.62$ ns (49%) and $\tau_2 = 4.43$ ns (51%)) exhibited a fast biexponential decay in the presence of 1.53 mol % of **13** with time constants of $\tau_1 = 0.72$ ns (56%) and $\tau_2 = 2.22$ ns (44%). This progressive shortening of the lifetime of **5a** in the presence of **13** indicates nonradiative energy transfer. The energy transfer is found to be more efficient in the gel state than in solution. The efficiency of energy transfer can be controlled by variation of the temperature, and thereby a white light emission was obtained at 54 °C.

A white-light-emitting organogel has been prepared by using a novel concept of functional-group-controlled donor self-assembly and the consequent modulation of excited-state properties in the supramolecular gel state.³¹ The difference in the excited-state dipole orientation of the OPV donors **14** and **15** (Figure 5) in the twisted and coiled helical states strongly influences the excited-state properties, particularly the excitation energy migration, as shown by the changes in the TRES data. The observed dynamic red-shift with time is an indication of the increased population of the singlet excited states of the higher-order aggregates with a low HOMO–LUMO energy gap through excitation energy migration. In the case of **14**, the red-shift was marginal, whereas for **15**, with increase in time after excitation, the emission spectrum becomes broad with a significant red-shift in the emission maximum. The strong gelation and fast exciton diffusion of **15** facilitate efficient energy transfer and lead to a red emission from the

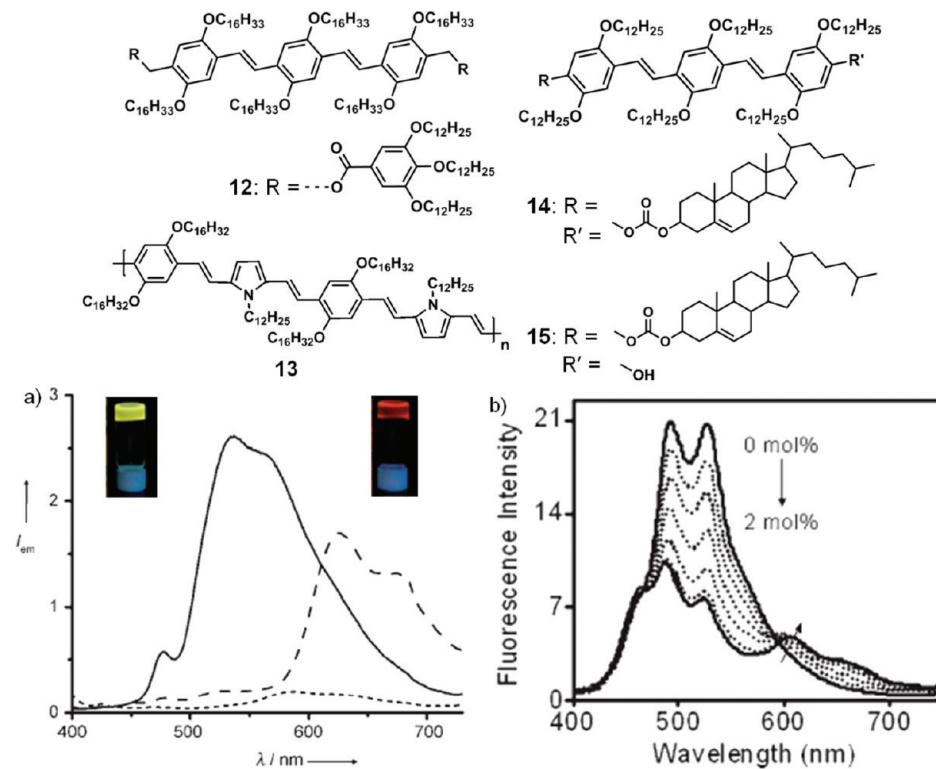


Figure 5. (a) Fluorescence spectrum of the 5a-cyclohexane gel ($c = 4 \times 10^{-4}$ M, $l = 1$ mm) in the absence (—) and in the presence (---) of 13 (1.53 mol %) and 13 alone (····) ($\lambda_{\text{ex}} = 380$ nm); inset shows the photographs of the corresponding emission color of the gels under illumination at 365 nm. (Reprinted with permission from ref 28. Copyright 2007 Wiley-VCH). (b) Fluorescence emission changes of *n*-decane gel of 14 ($c = 3.2 \times 10^{-4}$ M) in the presence of 0–2 mol % of 13 ($\lambda_{\text{ex}} = 380$ nm, $l = 1$ mm). Reprinted with permission from ref 31. Copyright 2009 Wiley-VCH.

acceptor **13** with a maximum of 90 % quenching of the donor emission. Because of the weak gelation in *n*-decane and slow exciton diffusion, a partial energy transfer occurred from the aggregates of **14** to the acceptor (Figure 5b) and at 2.1 mol % of **13**, which leads to the simultaneous generation of the RGB emission colors with CIE coordinates of (0.31, 0.35).

Recently, there has been renewed interest in the understanding of excited state properties of inorganic–organic hybrid systems.³² The formation of **5b**/16-Au (Figure 6) hybrid supramolecular tapes has been visualized by TEM analysis that showed arrays of Au particles on both sides of the tape, indicating the formation of supramolecular hybrid tapes of **5b**/16-Au. A hybrid gel of 100:1 **5b**/16-Au mixture in toluene resulted in the quenching of the OPV luminescence. The intensity was reduced by a factor of 33 in comparison with the emission intensity of **5b** alone. A shortening of the lifetime of **5b** in the presence of the nanoparticles indicates that the quenching is partly due to a dynamic process that takes place on a nanosecond time scale and involves diffusion of the electronic excitations through the tape toward the docked gold particles. A rapid energy transfer from **16**-Au to the gold core in the close proximity was further confirmed by a very short lifetime for **16**-Au system in the photoinduced absorption (PIA) studies for the S₁–Sn transition of the OPV chromophore ($\lambda_{\text{pump}} = 460$ nm and $\lambda_{\text{probe}} = 740$ nm). A clear difference in the population of the excited state for the

organic and hybrid gels indicates that the quenching due to rapid transfer of energy from OPV to the gold core is on the nanosecond time scale. The PIA studies have indicated that **5b** tapes and the bound **16**-Au particles interact electronically. This study highlights the importance of hybrid systems derived from π -conjugated molecules and inorganic nanoparticles in the design of new functional materials.

Concentration-dependent hierarchical self-assembly of a discotic 1,3,4-oxadiazole derivative **17** (Figure 6) and its photophysical properties has been reported by Das and co-workers.³³ Morphological studies of **17** have shown that hard spheres of nanometric dimensions have been observed at lower concentrations. The merging of these hard spheres at higher concentrations resulted in the formation of interlocked fibrils leading to gelation. This morphology transformation monitored by the changes in the fluorescence spectra revealed that the hexagonal columnar (Col_h) organization of **17** at lower concentrations predominantly form H-type of aggregates, whereas in the fibers, J-type of aggregates predominate. In the fibers, excitation led to red emission from the J-aggregate, indicating efficient energy transfer from the monomer and the H-aggregates to the J-aggregates (Figure 6a). Interestingly, the strong π – π interactions in the columnar organization of the disk-shaped chromophores within the fibers results in exciton migration from the H- to the J-type aggregates and subsequent emission from the J-traps. When compared to the lifetime of the monomer (0.82 ns), *n*-decane gels exhibited a

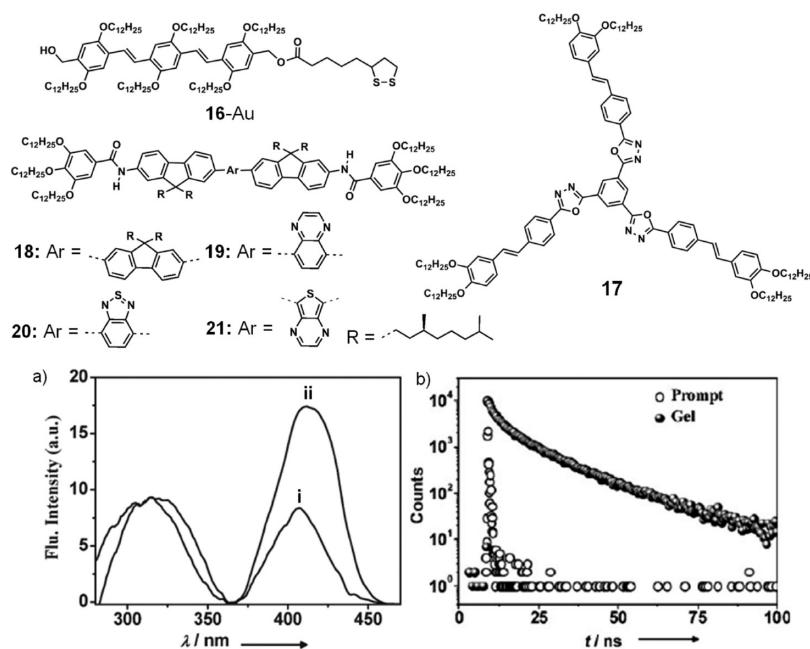


Figure 6. (a) Difference spectra obtained by subtracting the normalized excitation spectra of (i) 10^{-7} M from 10^{-6} M and (ii) 10^{-7} M from 2×10^{-5} M solutions of 17 in *n*-decane. (b) Fluorescence lifetime decay profile ($\lambda_{\text{ex}} = 375$ nm, $\lambda_{\text{em}} = 500$ nm). Reprinted with permission from ref 33. Copyright 2009 Wiley-VCH.

significantly higher lifetime of 17 ns, which is evidence of energy transfer in the gel state (Figure 6b).

Schenning and co-workers have reported partial energy transfer in a coassembly of four oligofluorenes with two chiral dialkylfluorene units having a central aromatic moiety (fluorene 18, quinoxaline 19, benzothiadiazole 20, and thiopyrazine 21), and connected to tris(dodecyloxy)benzene wedges using amide linkers to ensure hydrogen bonding and van der Waals interaction (Figure 6).³⁴ Interestingly, mixing small amounts of these derivatives with different emission colors, 19 (green), 20 (yellow), and 21 (red) into a gel of 18 in the molar ratio 18/19/20/21 = 0.7:0.2:0.1:4.5 resulted in partial energy transfer from the blue-emitting donor to the acceptors upon excitation of 18 leading to white-emitting gel. The fluorescence lifetime of the methylcyclohexane gel of 18 exhibited a biexponential decay with lifetimes of 0.93 (94.5%) and 1.81 ns (5.5%), whereas for the white-light-emitting gel, lifetime values were varied to 0.28 (95.4%) and 1.10 ns (5.6%), respectively.

Organogelation has been used to create 1D arrangement of molecularly interspaced donor/acceptor hybrid system through weak noncovalent interactions.³⁵ The gel fibers of 22 (Figure 7) in *o*-dichlorobenzene showed the formation of three-dimensional (3D) network structures, and aggregation of the molecules resulted in a blue-shift of 38 nm in the absorption spectrum and a decrease in intensity with red-shift in emission. The comparison of changes in emission intensity in the gel state of 22 upon addition of C₆₀ and C₆₀COOH derivative revealed a relatively effective quenching by the latter (Figure 7). This observation could be attributed to the better interaction of C₆₀COOH with the gelator and thereby resulting in a facile electron transfer. Hence, organogelation is crucial in making a good

connection and efficient charge separation between an electron donor and acceptor at the molecular level and thereby results in photocurrent.

Organogelation is crucial in making a good connection and efficient charge separation between an electron donor and acceptor.

Exciplex Formation and Enhanced Emission. An electronically excited electron donor–acceptor complex that is formed by the interaction of an excited molecular entity with a ground state counterpart of a different structure has been the subject of several studies.³⁶ When the exciplex returns to the ground state, its components dissociate and often repel each other. The wavelength of the exciplex emission is longer than that of the excited monomer's emission, and the lifetime of an exciplex is high compared to that of the monomer.³⁶ Hence, the formation of an exciplex could be monitored by steady state and time-resolved emissions changes.³⁷ Even though exciplex formation in different media has been extensively investigated, this phenomenon has not been seriously studied in gel medium. One of the main problems associated with gel forming fluorescent molecules is the fluorescence quenching in the gel state as observed in the case of OPV gelators. This phenomenon could be considerably

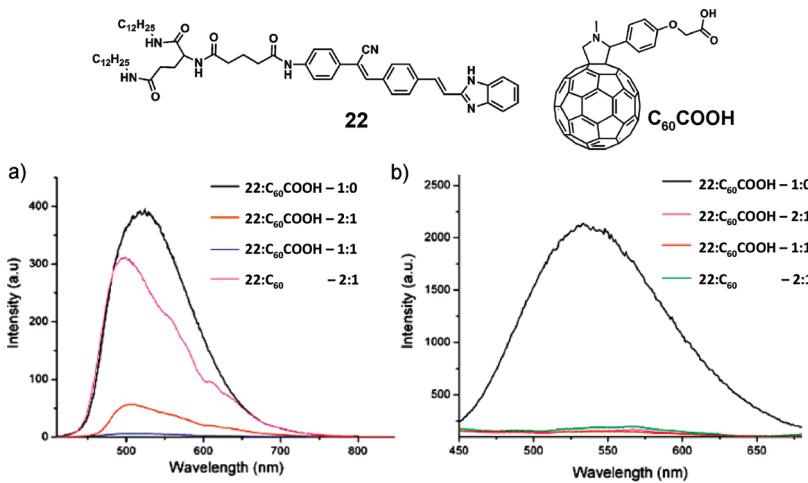


Figure 7. Fluorescence spectra of (a) wet gels and (b) xerogel films of 22 and hybrids ($c = 0.05$ wt/vol, $\lambda_{ex} = 400$ nm). Reprinted with permission from ref 35. Copyright 2010 American Chemical Society.

prevented by exciplex formation of the *n*-decane gel of **23** (Figure 8) with *N,N*-dimethylaniline (**DMA**).³⁸

Even though exciplex formation in different media has been extensively investigated, this phenomenon has not been seriously studied in gel medium.

The perfluoroarene-terminated OPV **23** forms gels from *n*-decane with significant quenching of the emission. Interestingly, the addition of **DMA** to the *n*-decane gel of **23** resulted in a considerable increase in the emission intensity at 580 nm, when compared to that of the *n*-decane gel of **23** alone (Figure 8a). The absorption spectrum of the gel did not vary much upon addition of **DMA**, indicating that the observed fluorescence enhancement is not due to the breaking of the self-assembly and there is no ground-state electronic interaction between **23** and **DMA** (Figure 8a, inset). The monoexponential fluorescence decay profile of **23** in the monomeric state (1.28 ns) is changed to biexponential decay with lifetimes of 0.82 and 3.26 ns (31 and 69%) in the exciplex gel. TRES also confirmed the formation of the exciplex gel, exhibiting a broad emission at $\lambda = 550$ nm after a time delay of 1.7 ns (Figure 8b). The intercalation of **DMA** in the brick-wall-type assembly of **23** in *n*-decane in the gel state allows proximity between the two moieties, which facilitates supramolecular exciplex formation when the latter is excited. Morphological studies of the *n*-decane gel in the presence and absence of **DMA** revealed that the presence of **DMA** in the OPV gel matrix does not have much influence on the gel morphology. A TEM image of **23** (5×10^{-5} M) in the presence of **DMA**

(0.5 M) in *n*-decane showed the formation of short, bundled fibrous assemblies with length of a few micrometers and width of 10–100 nm (Figure 8c). The intercalation of **DMA** in the brick-wall-type assembly of **23** in the gel state allows proximity between the two moieties, which facilitates supramolecular exciplex formation with enhanced emission (Figure 8c, inset). The fluorescence changes upon addition of **DMA** is clear from a comparison of the confocal laser scanning microscopic images of the gels of **23** before and after the addition of **DMA**.

Phosphorescent Organogels. Phosphorescence is a process in which energy absorbed by a molecule is released relatively slowly in the form of light.^{39,40} In a phosphorescent system, the absorbed photon energy undergoes an unusual intersystem crossing into an energy state of higher spin multiplicity usually a triplet state. Thus, the energy trapped in the triplet state (metastable state) returns to the lower energy singlet state through “forbidden” transitions, which are kinetically unfavored and thus progress at significantly slower time scales. If the phosphorescent quantum yield is high, the substance will release significant amounts of light over long time scales, creating the so-called “glow-in-the-dark” materials. Phosphorescent materials have gained much interest due to their advantages of long-lived luminescence and high luminescence quantum yield for various applications such as displays, sensors, photovoltaic devices and photocatalysts.³⁹

The platinum acetylide oligomers **24** and **25** (Figure 9) absorb light strongly in the near-UV, exhibit room-temperature phosphorescence from a long-lived triplet excited state, and provide an ideal platform for the study of triplet exciton transport and energy transfer.⁴¹ Supramolecular aggregates of **24** exhibit moderately intense blue-shifted (ca. 20 nm) phosphorescence from the platinum acetylide chromophore at ca. 500 nm at ambient temperature in solution and in the aggregate/gel state. The mixed aggregates of the host **24** and small amounts of **25** exhibited phosphorescence emission predominantly from the latter at ca. 600 nm via triplet exciton diffusion among the aggregates of **24** followed by energy transfer to the low energy acceptor **25** (Figure 9).

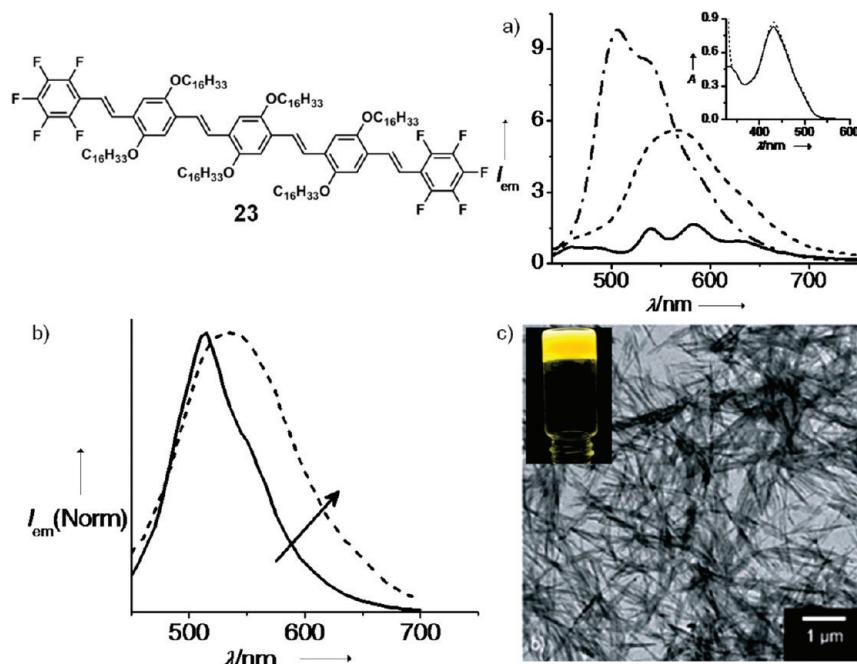


Figure 8. (a) Emission spectra of **23** (8.3×10^{-5} M) in *n*-decane at 20 °C (—), in *n*-decane at 65 °C (---), and in *n*-decane 0.83 M + DMA at 20 °C (— · —), ($\lambda_{\text{ex}} = 415$ nm). Inset shows the corresponding changes in the absorption spectra. (b) TRES of **23** in the presence of 0.83 M DMA at 56 ps (—) and 1.7 ns (— · —) after excitation at $\lambda = 440$ nm at 20 °C in *n*-decane (8.3×10^{-5} M). (c) TEM image (unstained) of **23** (5×10^{-5} M) in the presence of DMA (0.5 M) in *n*-decane; inset shows the photograph of the **23**+DMA gel in *n*-decane upon illumination with 365 nm light at 20 °C. Reprinted with permission from ref 38. Copyright 2008 Wiley VCH.

Aggregation-Induced Enhanced Emission. A number of molecules that are less emissive or nonemissive in solution show strong emission in the gel state due to AIEE phenomenon.^{42–47} This observation has generated considerable interest in research related to display devices, sensors, and so forth.^{48–51} There are several reasons for the enhanced emission in the aggregated state, including the presence of a forbidden band in H-aggregates, J-aggregate formation, planarization, and restriction of conformational flexibility. This section summarizes the recent reports in the field of AIEE.

There are several reasons for the enhanced emission in the aggregated state, including the presence of a forbidden band in H-aggregates, J-aggregate formation, planarization, and restriction of conformational flexibility.

in fluorescence intensity.⁴³ The fibrous aggregates of **26** are strongly fluorescent due to the enhanced emission in the aggregate state (Figure 10a). The gelation of **26** is attributed to the cooperative effect of the $\pi-\pi$ stacking interactions of the rigid rod-like aromatic segments and the supplementary intermolecular interactions induced by the four CF_3 units. In the aggregated gel state, molecules of **26** are likely to show drastically enhanced fluorescence emission when compared to those of isolated state due to intramolecular planarization and restricted excimer formation. This can be visualized from the photograph of the gel under UV illumination (Figure 10a, inset) and fluorescence microscopy images.

A transparent and fluorescent organogel was obtained through hydrogen bonding interaction between a nonfluorescent 2-(3',5'-bis-trifluoromethyl-biphenyl-4-yl)-3-(4-pyridin-4-yl-phenyl)-acrylonitrile **27** (Figure 10) and 3,5-bistrifluoromethyl benzoic acid.⁴⁴ The complexation of the monomer of **27** with a chiral sergeant, L-tartaric acid (L-TA) (or D-TA), also resulted in a stable gel, accompanied by a drastic fluorescence enhancement at 514 nm with an intensity 240 times that of the solution prior to gelation (Figure 10b). The AIEE effect originates from the combined planarization and J-type aggregation of molecules of **27** during aggregation.

A series of dumbbell-shaped dendritic molecules **28–30** (Figure 10) with a stiff aromatic *p*-terphenylene core and bulky dendritic wedges could form gels in organic solvents using amide hydrogen-bonded 1D aggregates.⁴⁵ AIEE (800 times) was observed for all three molecules upon gelation, whereas the solutions were nonfluorescent under the illumination of UV light. The combined effect of the planarization and reduced

Owing to their photoresponsive conformational changes, stilbenes are suitable moieties for the synthesis of “smart” gelators. The gelation of trifluoromethyl-based cyanostilbene derivative **26** (Figure 10) showed a considerable enhancement

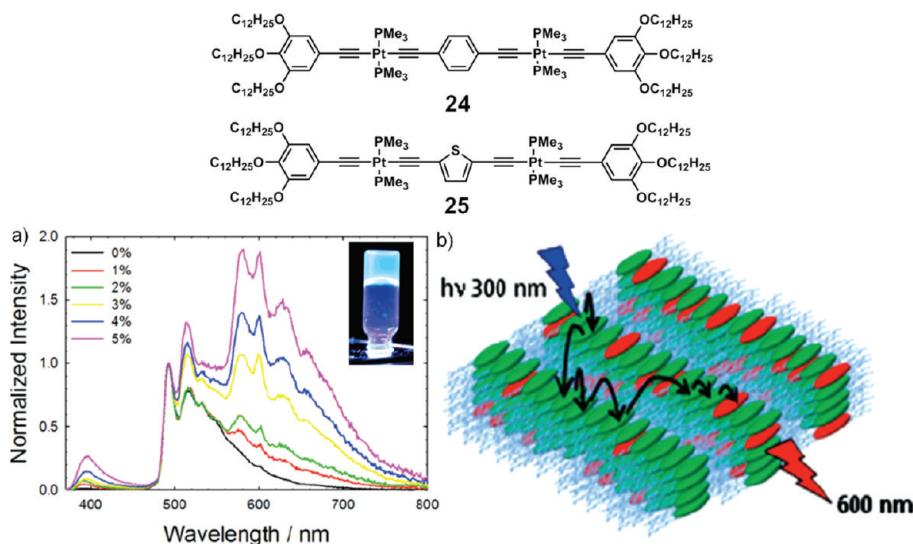


Figure 9. (a) Normalized photoluminescence spectra of mixed-oligomer gel of **24** (1×10^{-3} M) in deoxygenated dodecane at different mol % of **25** ($\lambda_{\text{ex}} = 300$ nm); inset shows the photograph of the dodecane gel of **24** (1 mM) under near-UV illumination. (b) Schematic representation of the exciton diffusion assisted energy transfer within the mixed aggregates. Reprinted with permission from ref 41. Copyright 2008 American Chemical Society.

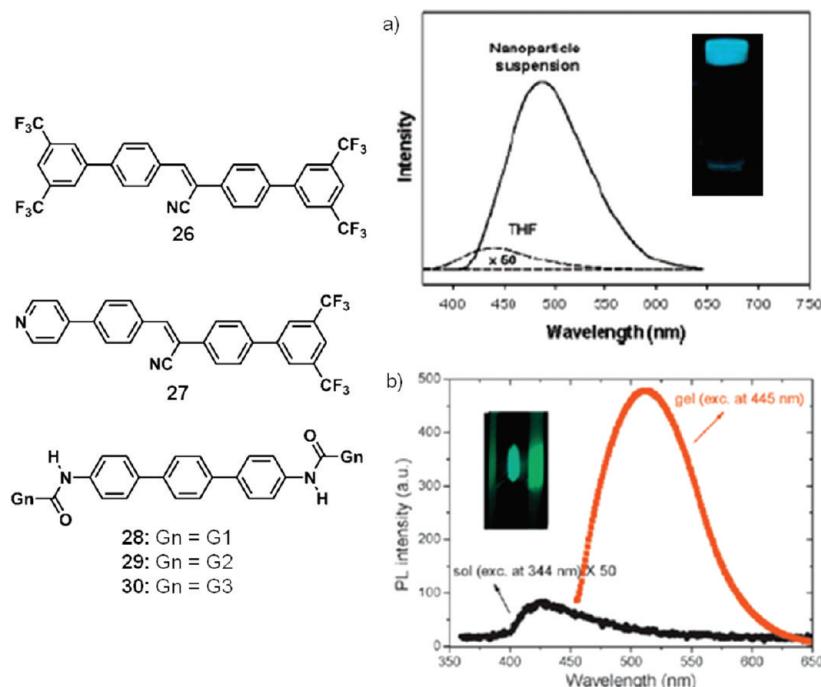


Figure 10. (a) Fluorescence spectra of **26** (2×10^{-5} mol L⁻¹) in tetrahydrofuran (THF) and its nanoparticle suspension (THF/water (1:4 mixture); inset shows the photograph of the 1,2-dichloroethane gel (0.8 wt/vol %)) (Reprinted with permission from ref 43. Copyright 2004 American Chemistry Society). (b) Photoluminescence spectra of **27** (0.25 wt %, 1 equiv.) in dichloroethane (black, sol) and in the presence of L-TA (0.5 equiv.) (red, gel) in THF (Reprinted with permission from ref 44. Copyright 2008 The Royal Society of Chemistry).

bond rotation within the *p*-terphenylene unit due to strong intermolecular hydrogen bonds leads to an enhancement in fluorescence in the gel state.

Tsou et al. have reported an example of a low molecular weight organogel derived from the phenyleneethynylthiophene derivative **31** (Figure 11) showing fluorescence enhance-

ments upon aggregation (Figure 11).⁴⁶ The fluorescence maximum of the dilute solution exhibited bathochromic shift to 506 and 523 nm, respectively, in gelling solution and film state. The variable temperature fluorescence spectra indicate the possibility of molecular aggregation through amide hydrogen bonding and/or π -stacking (Figure 11a).

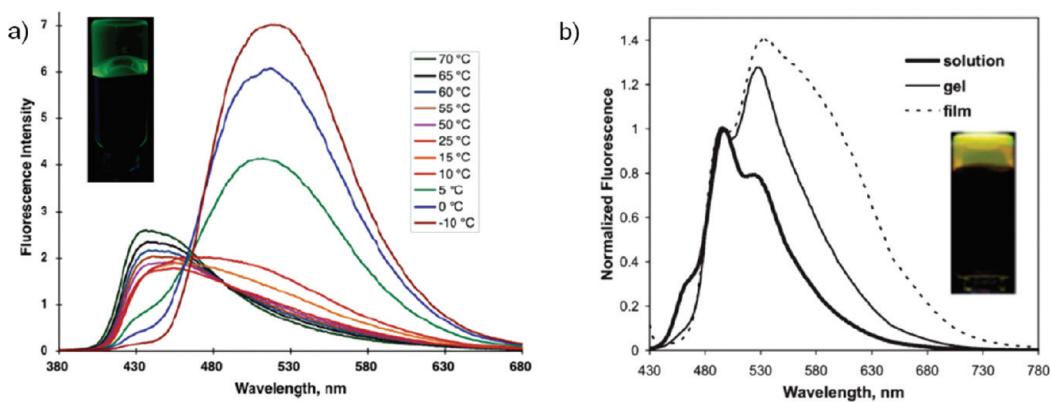
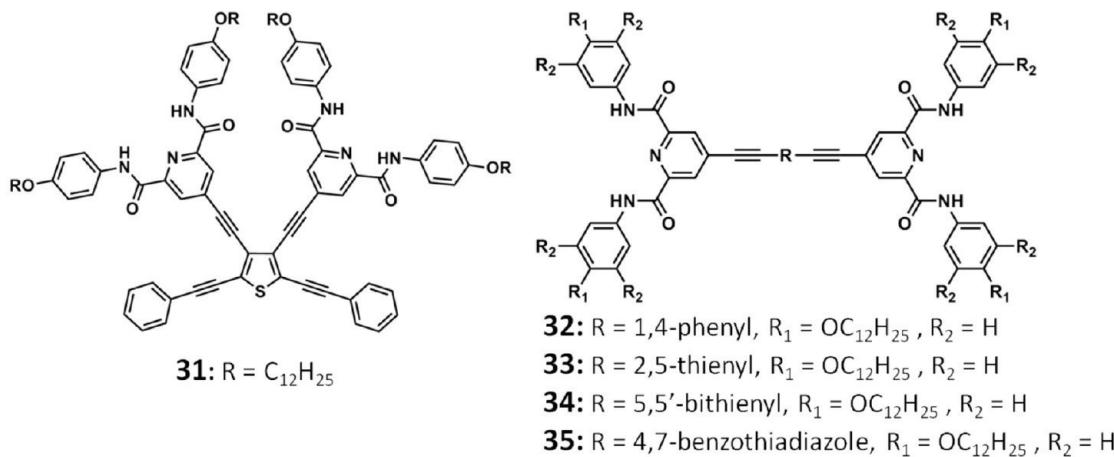


Figure 11. (a) Variable-temperature fluorescence spectra of **31** in toluene (1×10^{-5} M); inset shows a photograph of the gel of **31**. Reprinted with permission from ref 46. Copyright 2006 American Chemical Society. (b) Normalized fluorescence spectra of gelator **34** in dilute toluene (6.3×10^{-6} M), toluene gel (1 mM), and dried film at 293 K ($\lambda_{\text{ex}} = 420$ nm), inset shows a photograph of the toluene gel of **34** under UV illumination. Reprinted with permission from ref 47. Copyright 2009 American Chemical Society.

Sun et al. have recently shown the gelation property and enhanced emission of the phenylethynylene based gelators **32–35** (Figure 11).⁴⁷ The gelation of these compounds in nonpolar solvents results in the formation of aggregates due to strong intermolecular hydrogen bonding and $\pi-\pi$ interactions. The reduced conformational flexibility of the gelator slows down the nonradiative decay processes and leads to enhanced fluorescence quantum yields (Figure 11b). When compared to the solution state, toluene gels exhibit one order of higher quantum yields. Time-resolved emission studies revealed that the decrease in the nonradiative deactivation leads to the enhanced emission of the aggregates.

Conclusions and Outlook. Self-assembly of π -conjugated molecules to organogels is a suitable pathway to prepare soft materials having diverse architectures and size with tunable photophysical properties. Strong interactions between molecules in the gel state facilitate modulation of the electronic properties resulting in significant variation in absorption and emission spectra. The excited-state photophysical properties such as energy transfer, excimer formation, etc. are found to be efficient in the gel state, which can be reversibly controlled by temperature and polarity of the medium due to the reversible noncovalent interactions. The

concepts of AIEE and exciplex formation in the gel state are promising to prevent the usually encountered quenching of fluorescence in the aggregated state. These findings allow the design of self-assembled soft materials with tunable optical properties for a variety of applications. While energy transfer has been extensively studied in the gel state, in-depth investigation on electron transfer has not been reported in gel medium. Such investigations are important in the emerging field of organic solar cell research. Organo-gelation can be exploited for the creation of nanoarchitectures of donor–acceptor systems with efficient charge separation, useful for the construction of bulk heterojunction photovoltaic devices. In this context, rational design of functional organogels of p/n type organic semiconductors has tremendous potential in the field of organic electronics and smart materials for solar energy conversion and related applications.

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